ChE *classroom*

SPREADSHEETS FOR THERMODYNAMICS INSTRUCTION

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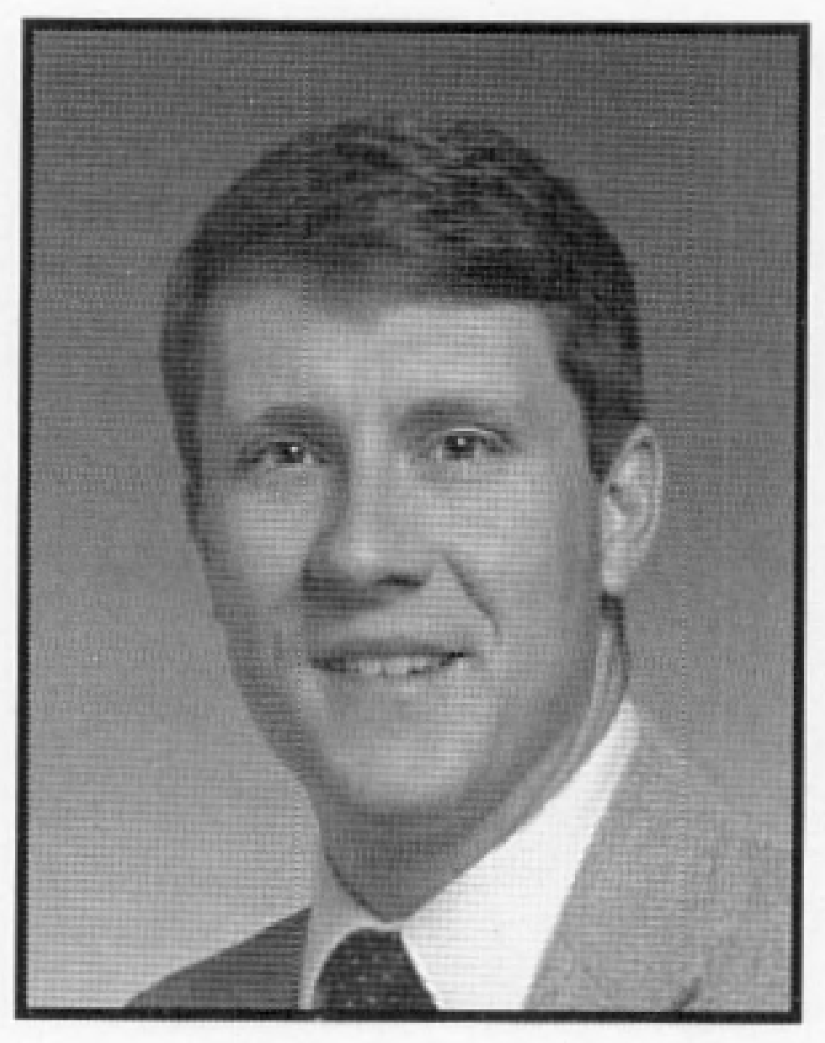
Thermodynamics, the study of energy, entropy, and equilibrium, is central to science and engineering. The laws of thermodynamics provide mathematical relationships that form the basis for understanding nature and for developing, analyzing, and optimizing chemical and physical processes. These relationships involve thermodynamic properties such as internal energy (U), enthalpy (H), entropy (S), Gibb's free energy (G), and fugacity (f). Numerical values of these properties must be determined for many different materials to solve engineering problems.

Equations of state (EOS), which relate the P-$\underline{V}$-T behavior of fluids, can be used to evaluate thermodynamic properties for many substances. For example, the specific molar enthalpy ($\underline{H}$) of a pure fluid can be computed from an EOS as

$$\underline{H}_{T,P} = RT(Z-1) + \int_{\infty}^{\underline{V}} \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \right] d\underline{V} + \int_{T_{ref}}^{T} C_p^{*} dT \qquad (1)$$

where the enthalpy was taken to be zero at an ideal-gas reference state of nearly zero pressure (infinite molar volume) and T_{ref}. To use Eq. (1) with an EOS, one must differentiate the pressure-explicit equation of state with respect to temperature at constant $\underline{V}$, then perform the integration over volume indicated in Eq. (1), and then finally solve the original EOS for the compressibility factor, Z, at the conditions of interest to determine the fluid's enthalpy at the conditions of interest. These mathematical manipulations become increasingly tedious as the form of the EOS become more complex.



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Keep in mind that Eq. (1) is completely general. It can be used with any EOS. This general approach is the one I emphasize in my thermodynamics classes. We use general expressions such as Eq. (1) and then evaluate the thermodynamic properties for a specific fluid of interest by employing an EOS that is valid for that fluid. In some cases, the ideal gas EOS ($P\underline{V} = RT$) can be used. Evaluating thermodynamic properties using the ideal gas law is simple. Compact, closed-form analytical expressions can be readily obtained for all thermodynamic properties. In other cases the ideal gas approximation is a poor one, but a generalized cubic EOS can be applied. Examples of generalized cubic EOS include the Peng-Robinson[1] and Soave-Redlich-Kwong[2] equations, shown below.

Peng-Robinson

$$P = \frac{RT}{\underline{V}-b} - \frac{a\alpha(T)}{\underline{V}^2 + 2b\underline{V} - b^2} \qquad (2)$$

Soave-Redlich-Kwong

$$P = \frac{RT}{\underline{V}-b} - \frac{a\alpha(T)}{\underline{V}(\underline{V}+b)} \qquad (3)$$

These are termed cubic EOS because they are cubic in $\underline{V}$ (or Z). This cubic form causes the mathematics associated with calculating thermodynamic properties to be tedious. Finally, in yet other cases, no cubic EOS is adequate and some other EOS or some other approach is required to evaluate thermodynamic properties.

One benefit of using the general approach described above is that it presents the ideal gas law as just another EOS, valid for some materials under certain conditions. It also removes the need to discuss thermodynamic properties for real fluids in terms of their departure from ideal gas behavior, a concept that is prevalent in thermodynamics texts. Departure functions (or residual properties) were popularized many years ago by the corresponding states charts for enthalpy and entropy.

Ideal gases are frequently used to introduce students to thermodynamics principles because the math does not get in the way of the thermodynamics. There are sound pedagogical reasons, however, for not emphasizing ideal gases to illustrate the evaluation of thermodynamic properties.[3,4] Feeding students a diet rich in ideal-gas examples and problems may leave the students ill prepared to analyze systems of practical interest where few fluids are ideal gases. Furthermore, an overemphasis of ideal gases gives students an unrealistic view of engineering applications. Finally, the exposure to ideal gases and the simplicity of the mathematics prove to be an irresistible temptation for some students, who treat every fluid they encounter as an ideal gas. Indeed, undergraduate students in my thermodynamics and reaction engineering classes have (on more than one occasion) used ideal-gas relationships to calculate thermodynamic property changes for high-pressure saturated steam and for liquids, fluids that are certainly not ideal gases!

My goal was to find a way to introduce non-ideal fluids during the early stages of the class' consideration of thermodynamic property estimation and to give the students hands-on experience with cubic EOS.

TABLE 1
Summary of Textbook Programs

Author	*Programs and Capabilities*
Sandler[8]	PR1.BAS: Peng-Robinson EOS for pure fluids VLMU.BAS: Peng Robinson EOS for mixture and multicomponent VLE calculations UNIFAC.BAS: Predict activity coefficients using UNIFAC CHEMEQ.BAS.: K_a as a function of temperature
Kyle[9]	PENGROB.BAS: Peng-Robinson EOS for pure fluids WILEQFIT.BAS: Use VLE data to find parameters in the Wilson equation
Sonntag & Van Wylen[7]	Corresponding states method to estimate Z and enthalpy and entropy departure functions

This firsthand exposure to a problem in thermodynamics instruction has motivated the work described in this paper. My goal was to find a way to introduce non-ideal fluids during the early stages of the class' consideration of thermodynamic property estimation and to give the students hands-on experience with cubic EOS. It is true that some thermodynamics texts[5-7] include diskettes with corresponding states methods and with thermodynamic properties for specific fluids such as steam and refrigerants, but only Sandler[8] and Kyle[9] include computer programs to calculate thermodynamics properties using a cubic EOS. (See Table 1 for a summary of existing programs for thermodynamics instruction involving equations of state.) It is also true, however, that some popular texts[10] do not include a diskette for EOS calculations. Moreover, I felt that using spreadsheets offers some unique advantages (more later) over these existing programs.

To this end, we developed computer spreadsheets (using Microsoft Excel) that students can easily use to calculate thermodynamics properties for real fluids using a generalized cubic EOS. Having these spreadsheets allows one to teach the general approach involved in evaluating thermodynamic properties without relying heavily on the ideal gas law. Moreover, the spreadsheets (and BASIC programs) equip the students to solve more realistic engineering problems.

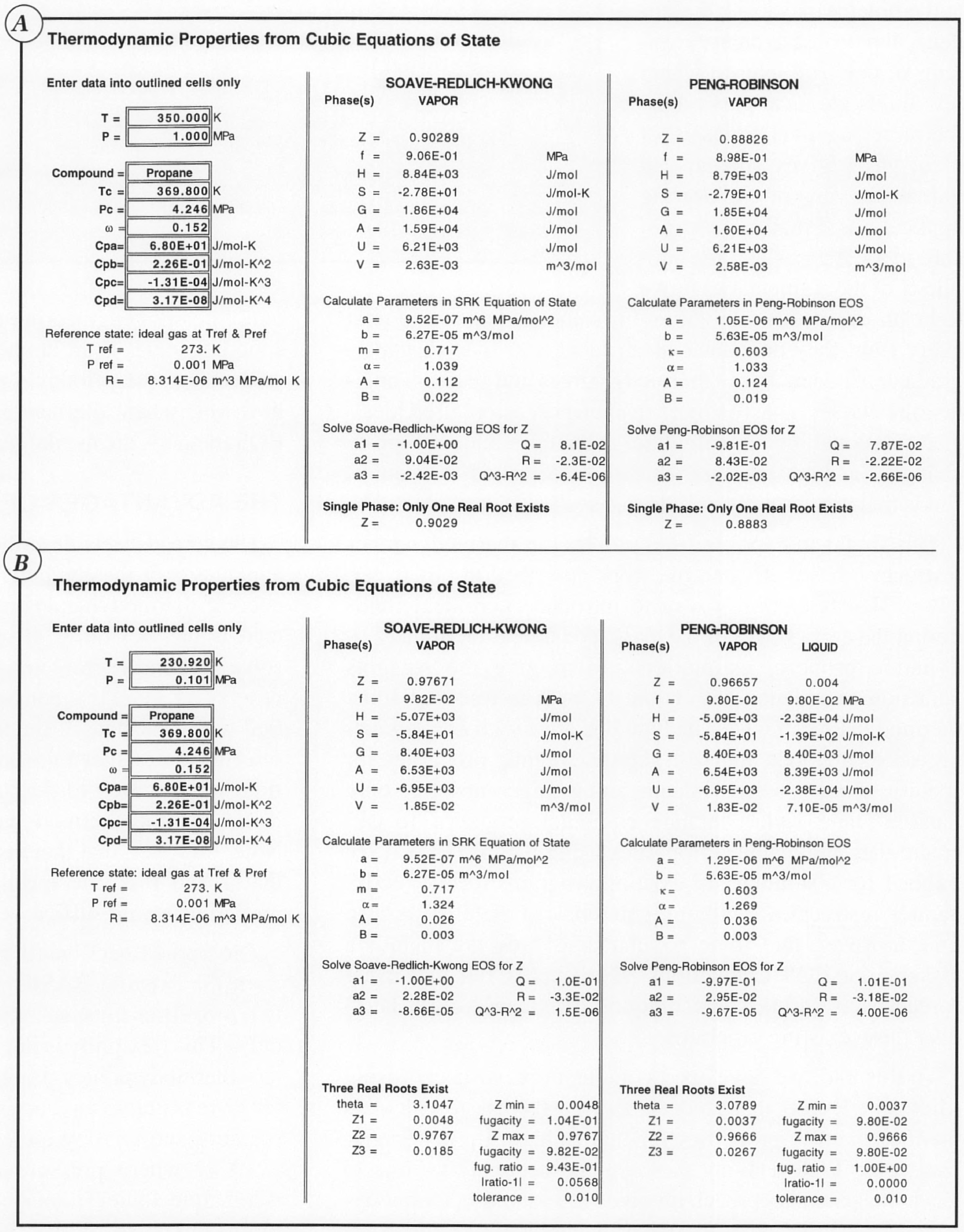
Previous generations of engineering students were taught to use the generalized corresponding states charts to evaluate properties for non-ideal fluids. These charts were developed in the 1940s, and they correlate thermodynamic properties for pure fluids as a function of the reduced pressure and temperature. Some implementations of this approach also use the critical compressibility or the acentric factor as a third correlating parameter. These charts certainly possess engineering utility, and the concept of corresponding states is an important one. We need not force our students to solve today's problems using 1940s methods, however, when alternative and more industrially relevant EOS methods are available.

THE ADVANTAGES OF SPREADSHEETS

The spreadsheets described herein have some unique advantages over the computer programs that accompany engineering thermodynamics texts. Perhaps the biggest advantage is the flexibility of spreadsheets and their ability to solve nonlinear problems. The existing textbook BASIC programs require that both temperature and pressure be specified to fix the state of the fluid. Of course, the Gibbs phase rule mandates that two properties of a pure single-phase fluid be specified to fix its state. After the state is established, all other thermodynamic properties can be calculated. Note, however, that there is no thermodynamic requirement that T and P be the specified properties. Indeed, *any* two properties would suffice.

The spreadsheet-based methods described herein differ from the existing BASIC programs in that they allow *any* two properties to be specified, not temperature and pressure only. This flexibility is important because one often encounters thermodynamics problems wherein the temperature or pressure is unknown. For example, cases are common where pressure and entropy are known (*e.g.*, isentropic compression) or where pressure and enthalpy are known (*e.g.*, isenthalpic Joule-Thomson expansion) but where temperature is unknown. With existing textbook programs, the student must adopt a manual trial-and-error procedure to find the temperature corresponding to this final state. With a spreadsheet, however, the student can specify any two known thermodynamic properties (*e.g.,* $\underline{S}$ and P) and then quickly find the temperature and all of the other properties using the spreadsheet's Solver algorithm.

Most commercial spreadsheet programs include a routine that one can use to solve for unknowns in an equation or set of equations. In Microsoft Excel (the program used to develop the spreadsheets described herein) this routine is named the Solver. This feature allows the user to specify a cell or set of cells whose numerical values are to be varied such that another cell achieves a specified value. The user can also place constraints on the solution. For example, an illustration that will appear later used the Solver to do a bubble point pressure calculation for a four-component mixture. The liquid composition and system temperature were known, and the vapor composition and system pressure were sought. The Solver varied the values of the system pressure and the vapor-phase mole fractions until the sum of these mole fractions was equal to unity and the constraints that the ratio of the vapor- to liquid-phase fugacities for each component had to equal unity were satisfied.



```
Thermodynamic Properties from Cubic Equations of State

Enter data into outlined cells only

        T =    350.000 K
        P =      1.000 MPa

 Compound =    Propane
       Tc =    369.800 K
       Pc =      4.246 MPa
        ω =      0.152
      Cpa=   6.80E+01 J/mol-K
      Cpb=   2.26E-01 J/mol-K^2
      Cpc=  -1.31E-04 J/mol-K^3
      Cpd=   3.17E-08 J/mol-K^4

Reference state: ideal gas at Tref & Pref
     T ref =           273. K
     P ref =          0.001 MPa
        R =    8.314E-06 m^3 MPa/mol K
```

```
              SOAVE-REDLICH-KWONG
Phase(s)         VAPOR

       Z =     0.90289
       f =    9.06E-01                 MPa
       H =    8.84E+03                 J/mol
       S =   -2.78E+01                 J/mol-K
       G =    1.86E+04                 J/mol
       A =    1.59E+04                 J/mol
       U =    6.21E+03                 J/mol
       V =    2.63E-03                 m^3/mol

Calculate Parameters in SRK Equation of State
       a =    9.52E-07 m^6  MPa/mol^2
       b =    6.27E-05 m^3/mol
       m =       0.717
       α =       1.039
       A =       0.112
       B =       0.022

Solve Soave-Redlich-Kwong EOS for Z
      a1 =   -1.00E+00           Q =    8.1E-02
      a2 =    9.04E-02           R =   -2.3E-02
      a3 =   -2.42E-03   Q^3-R^2 =   -6.4E-06

Single Phase: Only One Real Root Exists
       Z =      0.9029
```

```
              PENG-ROBINSON
Phase(s)         VAPOR

       Z =     0.88826
       f =    8.98E-01                 MPa
       H =    8.79E+03                 J/mol
       S =   -2.79E+01                 J/mol-K
       G =    1.85E+04                 J/mol
       A =    1.60E+04                 J/mol
       U =    6.21E+03                 J/mol
       V =    2.58E-03                 m^3/mol

Calculate Parameters in Peng-Robinson EOS
       a =    1.05E-06 m^6  MPa/mol^2
       b =    5.63E-05 m^3/mol
       κ =       0.603
       α =       1.033
       A =       0.124
       B =       0.019

Solve Peng-Robinson EOS for Z
      a1 =   -9.81E-01           Q =    7.87E-02
      a2 =    8.43E-02           R =   -2.22E-02
      a3 =   -2.02E-03   Q^3-R^2 =   -2.66E-06

Single Phase: Only One Real Root Exists
       Z =      0.8883
```

```
Thermodynamic Properties from Cubic Equations of State

Enter data into outlined cells only

        T =    230.920 K
        P =      0.101 MPa

 Compound =    Propane
       Tc =    369.800 K
       Pc =      4.246 MPa
        ω =      0.152
      Cpa=   6.80E+01 J/mol-K
      Cpb=   2.26E-01 J/mol-K^2
      Cpc=  -1.31E-04 J/mol-K^3
      Cpd=   3.17E-08 J/mol-K^4

Reference state: ideal gas at Tref & Pref
     T ref =           273. K
     P ref =          0.001 MPa
        R =    8.314E-06 m^3 MPa/mol K
```

```
              SOAVE-REDLICH-KWONG
Phase(s)         VAPOR

       Z =     0.97671
       f =    9.82E-02                 MPa
       H =   -5.07E+03                 J/mol
       S =   -5.84E+01                 J/mol-K
       G =    8.40E+03                 J/mol
       A =    6.53E+03                 J/mol
       U =   -6.95E+03                 J/mol
       V =    1.85E-02                 m^3/mol

Calculate Parameters in SRK Equation of State
       a =    9.52E-07 m^6  MPa/mol^2
       b =    6.27E-05 m^3/mol
       m =       0.717
       α =       1.324
       A =       0.026
       B =       0.003

Solve Soave-Redlich-Kwong EOS for Z
      a1 =   -1.00E+00           Q =    1.0E-01
      a2 =    2.28E-02           R =   -3.3E-02
      a3 =   -8.66E-05   Q^3-R^2 =    1.5E-06


Three Real Roots Exist
   theta =      3.1047       Z min =     0.0048
      Z1 =      0.0048    fugacity =   1.04E-01
      Z2 =      0.9767       Z max =     0.9767
      Z3 =      0.0185    fugacity =   9.82E-02
                          fug. ratio =  9.43E-01
                          lratio-1l =    0.0568
                          tolerance =     0.010
```

```
              PENG-ROBINSON
Phase(s)         VAPOR          LIQUID

       Z =     0.96657           0.004
       f =    9.80E-02        9.80E-02 MPa
       H =   -5.09E+03       -2.38E+04 J/mol
       S =   -5.84E+01       -1.39E+02 J/mol-K
       G =    8.40E+03        8.40E+03 J/mol
       A =    6.54E+03        8.39E+03 J/mol
       U =   -6.95E+03       -2.38E+04 J/mol
       V =    1.83E-02        7.10E-05 m^3/mol

Calculate Parameters in Peng-Robinson EOS
       a =    1.29E-06 m^6  MPa/mol^2
       b =    5.63E-05 m^3/mol
       κ =       0.603
       α =       1.269
       A =       0.036
       B =       0.003

Solve Peng-Robinson EOS for Z
      a1 =   -9.97E-01           Q =    1.01E-01
      a2 =    2.95E-02           R =   -3.18E-02
      a3 =   -9.67E-05   Q^3-R^2 =    4.00E-06


Three Real Roots Exist
   theta =      3.0789       Z min =     0.0037
      Z1 =      0.0037    fugacity =   9.80E-02
      Z2 =      0.9666       Z max =     0.9666
      Z3 =      0.0267    fugacity =   9.80E-02
                          fug. ratio =  1.00E+00
                          lratio-1l =    0.0000
                          tolerance =     0.010
```

Figure 1. *Properties of propane from cubic equations of state:* ***a)*** *at 350K and 10 bar* ***b)*** *at the normal boiling point as determined from the Peng-Robinson EOS*

A second advantage of spreadsheets over computer codes is that our undergraduate students have extensive experience with spreadsheets. This familiarity and a spreadsheet's open structure enable students to look at the formula in a given cell and see the equation used and the information required to use it. The student can gain an appreciation for the methods behind the calculations. They also have the opportunity to modify the spreadsheet.

To summarize, the existing BASIC programs are available only with specific textbooks, and some popular texts do not include any programs at all. The spreadsheets described in this paper are not text specific. They can be used in conjunction with any engineering thermodynamics text. Copies of the spreadsheets are available from the author. Although developed with Microsoft Excel, the spreadsheets can also be read by other popular spreadsheet programs. Finally, the spreadsheets described herein can solve a wider variety of thermodynamics problems than can any of the existing textbook programs.

DESCRIPTION OF THE SPREADSHEETS

This paper describes three different spreadsheets for thermodynamics instruction. One calculates thermodynamic properties for a pure fluid using both the Peng-Robinson and the

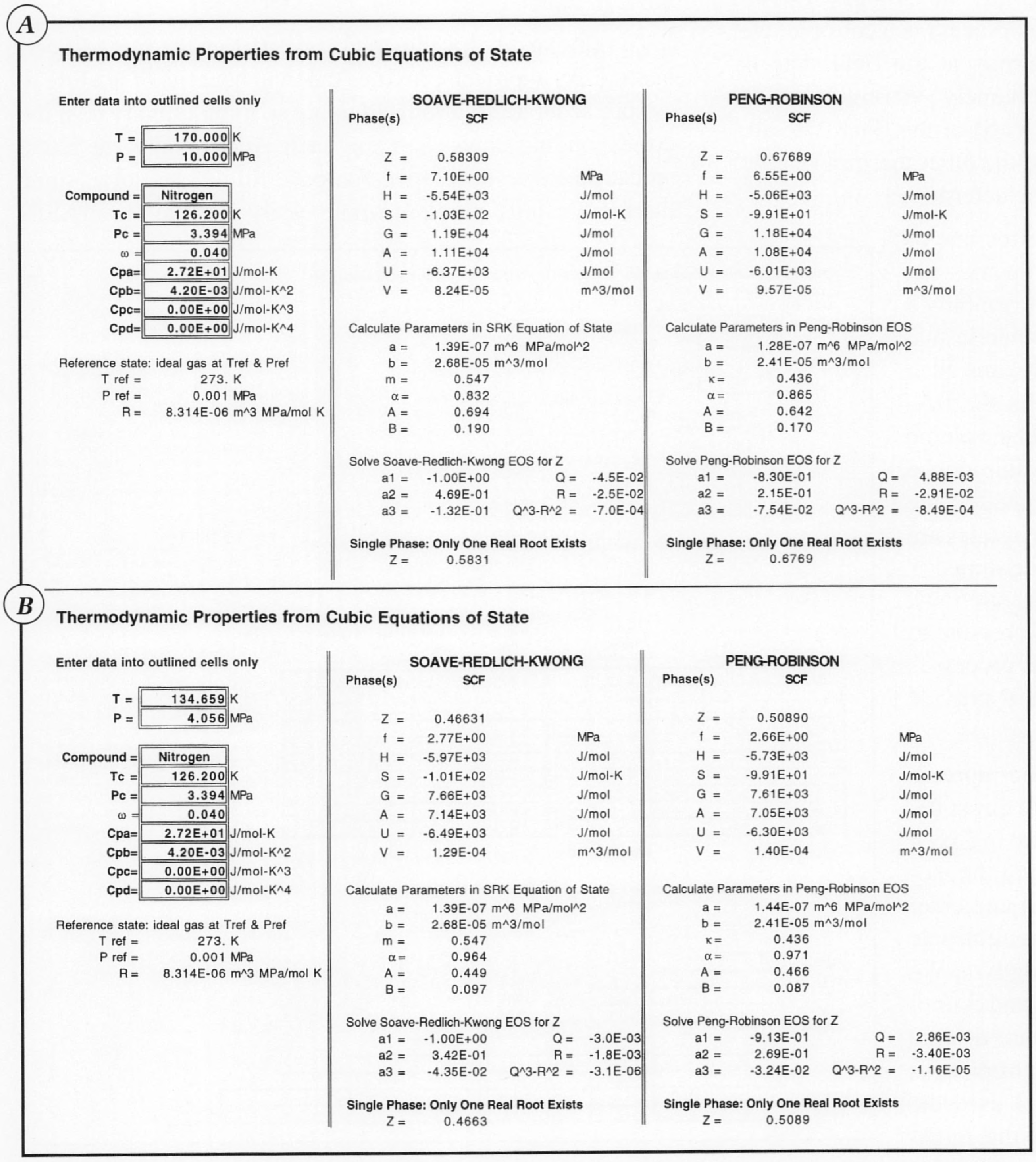
Soave-Redlich-Kwong EOS. The second spreadsheet, which is an extension of the first, calculates thermodynamic properties for mixtures using the Peng-Robinson EOS. The final spreadsheet performs chemical equilibrium calculations for single reactions occurring in ideal and non-ideal fluid phases. Each of these spreadsheets is described in more detail in the following subsections.

Pure Fluids

Figure 1 displays the spreadsheet that calculates pure-component thermodynamics properties. In this and all subsequent figures, the cell gridlines and the column and row headings were not printed. The user enters values for two properties (say T and P), and then provides data (T_c. P_c, ω, and the constants in the ideal gas heat capacity equation $C_p^*(T)=a+bT+cT^2+dT^3$) for the fluid of interest. The spreadsheet then uses an analytical solution for the cubic equation to calculate the value(s) of Z that satisfy the EOS. The value of Z is then used to compute all of the thermodynamic properties for the fluid. Figure 1a shows results of these calculations for propane at 350K and 10 bar, which is a pure vapor at these conditions.

When multiple real roots exist for the cubic EOS, the spreadsheet calculates the fugacity corresponding to the highest and lowest value of Z. If these fugacities are equal (to within a user-specified tolerance), then two phases exist and the spreadsheet provides all of the properties for each phase (see Peng-Robinson results in Figure 1b). This ability to identify vapor-liquid equilibrium conditions provides a convenient means of estimating vapor pressures, saturation temperatures, and heats of vaporization from an EOS. For example, the results in Figure 1b were obtained by setting the pressure to 0.101325 MPa (1 atm) and using the Solver to find the temperature that resulted in the fugacities in the two phases being equal. This temperature, of course, is the normal boiling point, given as 231.1 K for propane.[8] The normal boiling point of 230.9 K estimated by the Peng-Robinson EOS is in good agreement.

If there are multiple real roots in the cubic EOS and the fugacities corresponding to the highest and lowest value of Z are not equal, then but a single phase exists. The spreadsheet selects the value of Z that gives the lower fugacity as the correct root (see Soave-Redlich-Kwong results in Figure 1b). The spreadsheet also checks for values of Z less than zero and rejects these as possible solutions to the EOS.



```
Thermodynamic Properties from Cubic Equations of State

Enter data into outlined cells only        SOAVE-REDLICH-KWONG                         PENG-ROBINSON
                                     Phase(s)      SCF                          Phase(s)      SCF
        T =    170.000 K
        P =     10.000 MPa                Z =    0.58309                              Z =    0.67689
                                          f =   7.10E+00           MPa                f =   6.55E+00           MPa
 Compound =   Nitrogen                    H =  -5.54E+03           J/mol              H =  -5.06E+03           J/mol
       Tc =    126.200 K                  S =  -1.03E+02           J/mol-K            S =  -9.91E+01           J/mol-K
       Pc =      3.394 MPa                G =   1.19E+04           J/mol              G =   1.18E+04           J/mol
        ω =      0.040                    A =   1.11E+04           J/mol              A =   1.08E+04           J/mol
      Cpa=    2.72E+01 J/mol-K            U =  -6.37E+03           J/mol              U =  -6.01E+03           J/mol
      Cpb=    4.20E-03 J/mol-K^2          V =   8.24E-05           m^3/mol            V =   9.57E-05           m^3/mol
      Cpc=    0.00E+00 J/mol-K^3
      Cpd=    0.00E+00 J/mol-K^4     Calculate Parameters in SRK Equation of State  Calculate Parameters in Peng-Robinson EOS
                                          a =   1.39E-07 m^6  MPa/mol^2               a =   1.28E-07 m^6  MPa/mol^2
Reference state: ideal gas at Tref & Pref b =   2.68E-05 m^3/mol                      b =   2.41E-05 m^3/mol
     T ref =          273. K              m =      0.547                              κ =      0.436
     P ref =         0.001 MPa            α =      0.832                              α =      0.865
         R =   8.314E-06 m^3 MPa/mol K    A =      0.694                              A =      0.642
                                          B =      0.190                              B =      0.170

                                     Solve Soave-Redlich-Kwong EOS for Z            Solve Peng-Robinson EOS for Z
                                         a1 =  -1.00E+00          Q =  -4.5E-02      a1 =  -8.30E-01          Q =   4.88E-03
                                         a2 =   4.69E-01          R =  -2.5E-02      a2 =   2.15E-01          R =  -2.91E-02
                                         a3 =  -1.32E-01  Q^3-R^2 =  -7.0E-04      a3 =  -7.54E-02  Q^3-R^2 =  -8.49E-04

                                     Single Phase: Only One Real Root Exists        Single Phase: Only One Real Root Exists
                                          Z =     0.5831                              Z =     0.6769
```

```
Thermodynamic Properties from Cubic Equations of State

Enter data into outlined cells only        SOAVE-REDLICH-KWONG                         PENG-ROBINSON
                                     Phase(s)      SCF                          Phase(s)      SCF
        T =    134.659 K
        P =      4.056 MPa                Z =    0.46631                              Z =    0.50890
                                          f =   2.77E+00           MPa                f =   2.66E+00           MPa
 Compound =   Nitrogen                    H =  -5.97E+03           J/mol              H =  -5.73E+03           J/mol
       Tc =    126.200 K                  S =  -1.01E+02           J/mol-K            S =  -9.91E+01           J/mol-K
       Pc =      3.394 MPa                G =   7.66E+03           J/mol              G =   7.61E+03           J/mol
        ω =      0.040                    A =   7.14E+03           J/mol              A =   7.05E+03           J/mol
      Cpa=    2.72E+01 J/mol-K            U =  -6.49E+03           J/mol              U =  -6.30E+03           J/mol
      Cpb=    4.20E-03 J/mol-K^2          V =   1.29E-04           m^3/mol            V =   1.40E-04           m^3/mol
      Cpc=    0.00E+00 J/mol-K^3
      Cpd=    0.00E+00 J/mol-K^4     Calculate Parameters in SRK Equation of State  Calculate Parameters in Peng-Robinson EOS
                                          a =   1.39E-07 m^6  MPa/mol^2               a =   1.44E-07 m^6  MPa/mol^2
Reference state: ideal gas at Tref & Pref b =   2.68E-05 m^3/mol                      b =   2.41E-05 m^3/mol
     T ref =          273. K              m =      0.547                              κ =      0.436
     P ref =         0.001 MPa            α =      0.964                              α =      0.971
         R =   8.314E-06 m^3 MPa/mol K    A =      0.449                              A =      0.466
                                          B =      0.097                              B =      0.087

                                     Solve Soave-Redlich-Kwong EOS for Z            Solve Peng-Robinson EOS for Z
                                         a1 =  -1.00E+00          Q =  -3.0E-03      a1 =  -9.13E-01          Q =   2.86E-03
                                         a2 =   3.42E-01          R =  -1.8E-03      a2 =   2.69E-01          R =  -3.40E-03
                                         a3 =  -4.35E-02  Q^3-R^2 =  -3.1E-06      a3 =  -3.24E-02  Q^3-R^2 =  -1.16E-05

                                     Single Phase: Only One Real Root Exists        Single Phase: Only One Real Root Exists
                                          Z =     0.4663                              Z =     0.5089
```

Figure 2. *Spreadsheets with properties of N_2 used to solve Illustration 4.7-1 in Sandler:* ***a)*** *at the initial conditions, and* ***b)*** *at the final conditions.*

As noted previously, one of the advantages of spreadsheets over existing BASIC programs is their ability to solve problems wherein T or P is one of the unknowns. To illustrate this capability, we will use the spreadsheet to do Illustration 4.7-1 on page 184 of Sandler's text.[8] This problem involves the removal of 10 mol/min of N_2 from a 0.15 m^3 gas cylinder initially at 100 bar and 170K. The student is given the ideal gas heat capacity equation as

$$C_p^*(\text{J / mol K}) = 27.2 + 4.2\times10^{-3}(\text{T in K})$$

and is asked to use the Peng-Robinson EOS to find the temperature and pressure and the number of moles of N_2 in the cylinder after 50 minutes.

The number of moles remaining after 50 minutes is readily calculated from a mass balance after the initial number of moles present has been determined from a knowledge of the tank volume and the molar volume of the gas at the initial conditions. Figure 2a shows the spreadsheet with the T and P corresponding to the initial conditions. The molar volume is 9.567×10^{-5} m^3/mol, which leads to 1567.9 moles of N_2 being present initially and 1067.9 moles of N_2 being present after 50 minutes. Therefore, the molar volume of the gas in the cylinder after the expansion is 0.15 m^3/1067.9 mol = 1.4046×10^{-4} m^3/mol. Moreover, since the process is isentropic, we know that the specific molar entropy at the final state is equal to that of the initial state, namely -99.069 J/mol-K. Two thermodynamic properties ($\underline{V}$, $\underline{S}$) of the final state are now known, so, in principle, all of the other thermodynamic properties (such as T and P) can be determined.

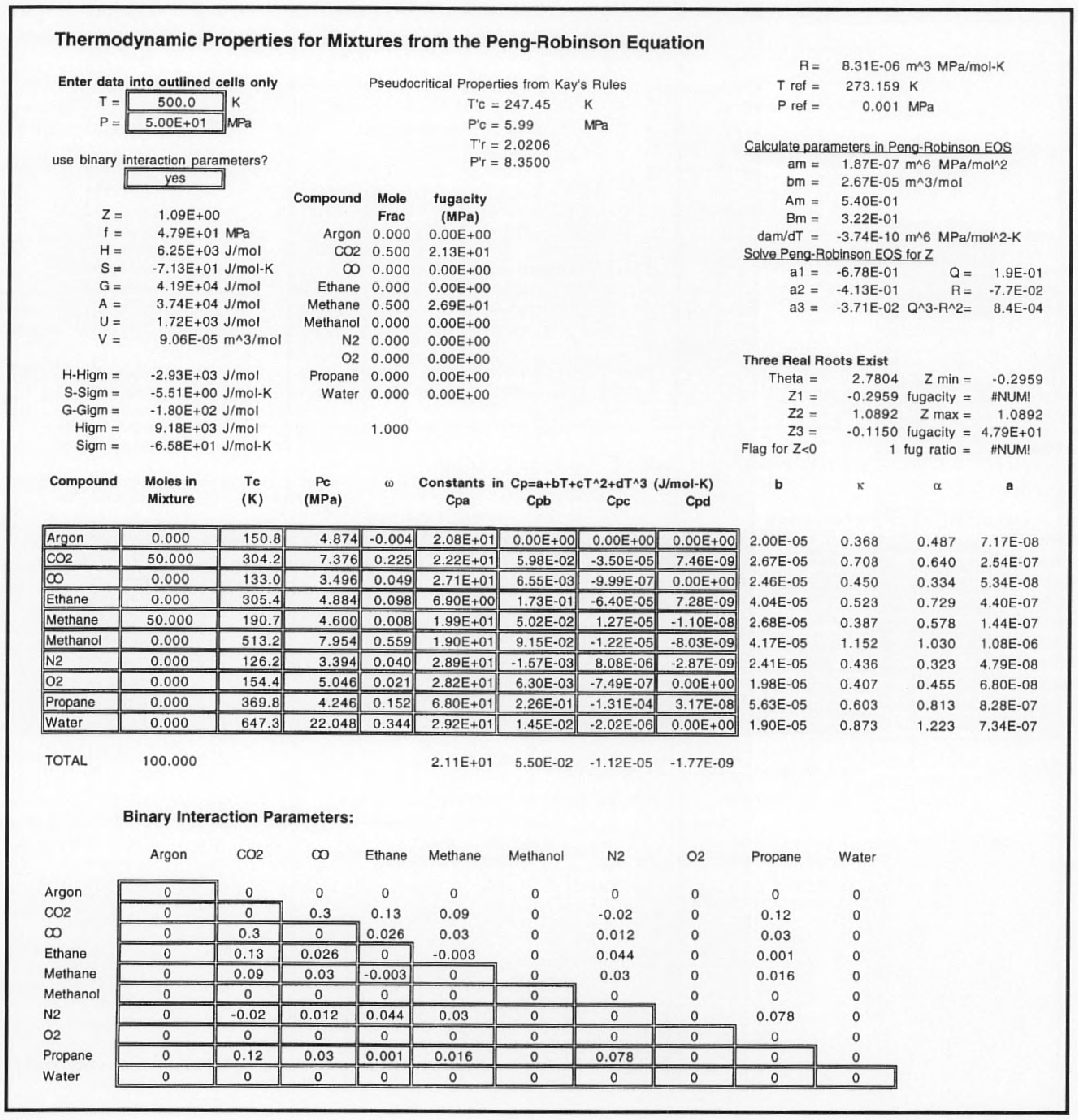
The solution in Sandler's text uses one of the BASIC programs that accompanies his text. The suggested procedure is to employ a nested trial-and-error approach wherein one first guesses the final temperature, and then varies the final pressure entered in the BASIC program until the desired molar volume is obtained. Next, one uses the value of the entropy departure function calculated at the final state to check whether the two states are truly isentropic. If they are, the assumed T and P are correct. If they are not, one must guess a new T and again vary the pressure to get the correct molar volume. This process is repeated until the assumed T and P provide the desired values of $\underline{V}$ and $\underline{S}$.

The solution procedure using our spreadsheet is simpler, quicker, and more direct because one can use the Solver feature in Excel. Here we specify the desired value of the molar volume (1.4046×10^{-4} m^3/mol) and enter the requirement that the process be isentropic as a constraint in the Solver Dialog box. We then instruct the Solver to vary T and P until the molar volume attains the value desired and such that the process is isentropic. As Sandler did in Illustration 4.7-1, I used the ideal gas results for T and P as the initial guesses. The Solver converged to the solution in 30 seconds (on a Mac IIsi), and Figure 2b displays the results. No manual trial-and-error was involved.

We note that the results given in Figure 2b (T=134.7K, P=40.56 bar) differ from those given as the solution in Illustration 4.7-1 (T=143.6K, P=48.6 bar). The solution in the text is incorrect because the same pair of state variables was not used consistently throughout the entire solution.

We also note that the T and P obtained from the Peng-Robinson EOS are closer to the values (138K, 41 bar) determined from a thermodynamic property chart for N_2 than are the values determined from the corresponding states charts. Using a more complete ideal gas heat capacity equation improves the agreement even further. Moreover, the corresponding states charts are tedious to use for this problem (see Illustrations 4.5-1 and 4.6-2 in Sandler).

To summarize, this illustration shows that the spreadsheet-based EOS approach provides the twin benefits of leading to a more accurate solution and doing so more quickly than the corresponding states chart approach. Additionally, the Excel spreadsheet we developed for pure fluids can solve some thermodynamics problems more easily than can the BASIC



Thermodynamic Properties for Mixtures from the Peng-Robinson Equation

Enter data into outlined cells only
T = 500.0 K
P = 5.00E+01 MPa

use binary interaction parameters?
yes

Pseudocritical Properties from Kay's Rules
T'c = 247.45 K
P'c = 5.99 MPa
T'r = 2.0206
P'r = 8.3500

R = 8.31E-06 m^3 MPa/mol-K
T ref = 273.159 K
P ref = 0.001 MPa

Z = 1.09E+00
f = 4.79E+01 MPa
H = 6.25E+03 J/mol
S = -7.13E+01 J/mol-K
G = 4.19E+04 J/mol
A = 3.74E+04 J/mol
U = 1.72E+03 J/mol
V = 9.06E-05 m^3/mol

H-Higm = -2.93E+03 J/mol
S-Sigm = -5.51E+00 J/mol-K
G-Gigm = -1.80E+02 J/mol
Higm = 9.18E+03 J/mol
Sigm = -6.58E+01 J/mol-K

Compound	Mole Frac	fugacity (MPa)
Argon	0.000	0.00E+00
CO2	0.500	2.13E+01
CO	0.000	0.00E+00
Ethane	0.000	0.00E+00
Methane	0.500	2.69E+01
Methanol	0.000	0.00E+00
N2	0.000	0.00E+00
O2	0.000	0.00E+00
Propane	0.000	0.00E+00
Water	0.000	0.00E+00
	1.000	

Calculate parameters in Peng-Robinson EOS
am = 1.87E-07 m^6 MPa/mol^2
bm = 2.67E-05 m^3/mol
Am = 5.40E-01
Bm = 3.22E-01
dam/dT = -3.74E-10 m^6 MPa/mol^2-K

Solve Peng-Robinson EOS for Z
a1 = -6.78E-01 Q = 1.9E-01
a2 = -4.13E-01 R = -7.7E-02
a3 = -3.71E-02 Q^3-R^2= 8.4E-04

Three Real Roots Exist
Theta = 2.7804 Z min = -0.2959
Z1 = -0.2959 fugacity = #NUM!
Z2 = 1.0892 Z max = 1.0892
Z3 = -0.1150 fugacity = 4.79E+01
Flag for Z<0 1 fug ratio = #NUM!

Compound	**Moles in Mixture**	**Tc (K)**	**Pc (MPa)**	ω	**Constants in Cp=a+bT+cT^2+dT^3 (J/mol-K)** Cpa	Cpb	Cpc	Cpd	b	κ	α	a
Argon	0.000	150.8	4.874	-0.004	2.08E+01	0.00E+00	0.00E+00	0.00E+00	2.00E-05	0.368	0.487	7.17E-08
CO2	50.000	304.2	7.376	0.225	2.22E+01	5.98E-02	-3.50E-05	7.46E-09	2.67E-05	0.708	0.640	2.54E-07
CO	0.000	133.0	3.496	0.049	2.71E+01	6.55E-03	-9.99E-07	0.00E+00	2.46E-05	0.450	0.334	5.34E-08
Ethane	0.000	305.4	4.884	0.098	6.90E+00	1.73E-01	-6.40E-05	7.28E-09	4.04E-05	0.523	0.729	4.40E-07
Methane	50.000	190.7	4.600	0.008	1.99E+01	5.02E-02	1.27E-05	-1.10E-08	2.68E-05	0.387	0.578	1.44E-07
Methanol	0.000	513.2	7.954	0.559	1.90E+01	9.15E-02	-1.22E-05	-8.03E-09	4.17E-05	1.152	1.030	1.08E-06
N2	0.000	126.2	3.394	0.040	2.89E+01	-1.57E-03	8.08E-06	-2.87E-09	2.41E-05	0.436	0.323	4.79E-08
O2	0.000	154.4	5.046	0.021	2.82E+01	6.30E-03	-7.49E-07	0.00E+00	1.98E-05	0.407	0.455	6.80E-08
Propane	0.000	369.8	4.246	0.152	6.80E+01	2.26E-01	-1.31E-04	3.17E-08	5.63E-05	0.603	0.813	8.28E-07
Water	0.000	647.3	22.048	0.344	2.92E+01	1.45E-02	-2.02E-06	0.00E+00	1.90E-05	0.873	1.223	7.34E-07
TOTAL	100.000				2.11E+01	5.50E-02	-1.12E-05	-1.77E-09				

Binary Interaction Parameters:

	Argon	CO2	CO	Ethane	Methane	Methanol	N2	O2	Propane	Water
Argon	0	0	0	0	0	0	0	0	0	0
CO2	0	0	0.3	0.13	0.09	0	-0.02	0	0.12	0
CO	0	0.3	0	0.026	0.03	0	0.012	0	0.03	0
Ethane	0	0.13	0.026	0	-0.003	0	0.044	0	0.001	0
Methane	0	0.09	0.03	-0.003	0	0	0.03	0	0.016	0
Methanol	0	0	0	0	0	0	0	0	0	0
N2	0	-0.02	0.012	0.044	0.03	0	0	0	0.078	0
O2	0	0	0	0	0	0	0	0	0	0
Propane	0	0.12	0.03	0.001	0.016	0	0.078	0	0	0
Water	0	0	0	0	0	0	0	0	0	0

Figure 3. *Properties of mixtures from the Peng-Robinson EOS with solution to Illustration 7.7-2 in Sandler.*

programs that accompany some thermodynamics texts.

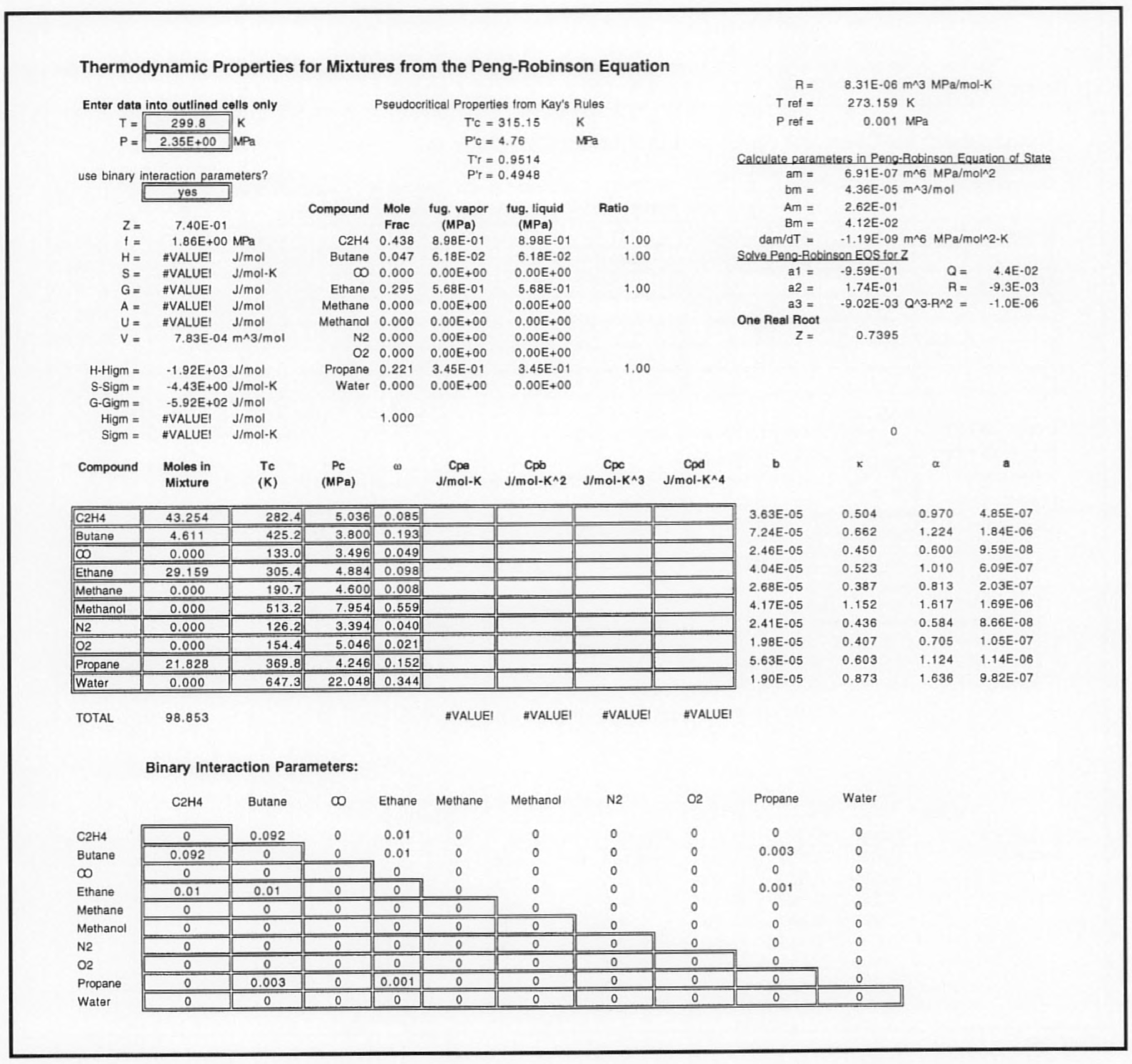
Fluid Mixtures

The second spreadsheet we developed uses the Peng-Robinson EOS to calculate thermodynamic properties for mixtures. It is an extension of the spreadsheet described above for pure fluids. In its current form, the mixtures spreadsheet can handle up to 10 components. Figure 3 displays the mixtures spreadsheet, with substances often encountered in combustion problems as the components in the mixture. Of course, the user is free to specify any set of compounds of interest. The user must supply the number of moles and T_c, P_c, and ω, for each component, as well as the constants in the ideal gas heat capacity equation. The spreadsheet will also incorporate binary interaction parameters, and the user should enter these when they are available. The spreadsheet calculates all of the thermodynamic properties of the fluid mixture and also calculates the fugacity for each of the individual components in the mixture. Pseudo-critical values are displayed, as are the values of the enthalpy and entropy departure functions. Figure 3 displays the solution to Illustration 7.7-2 in Sandler, which involves estimating the fugacity of each component in a equimolar binary mixture.

In addition to calculating thermodynamic properties, the mixtures spreadsheet can also be used as the basis for solving problems such as isothermal flash calculations and dew point and bubble point determinations. For example, one can tackle a problem with two phases present by linking two copies of the spreadsheet: one for the liquid phase and the second for the vapor phase.

I used this approach to solve Example 9-6 in Kyle.[9] The problem is to calculate the bubble point pressure and vapor composition for a mixture of ethane, ethylene, propane, and butane given the liquid-phase composition and the system temperature. One can link the spreadsheets such that the pressure entered in the spreadsheet for the vapor phase also appears as the pressure in the spreadsheet for the liquid phase. After this pressure is specified, one can calculate the fugacities of all of the liquid-phase components. These liquid-phase fugacities were then copied to and linked with the vapor-phase spreadsheet so they could be compared with the vapor-phase fugacities for the same components.

After the spreadsheets for the two phases were linked as just described, I entered initial guesses for the vapor-phase mole fractions. I then instructed the Solver to vary these vapor compositions and the pressure until the vapor mole fractions summed to unity subject to the constraints that the ratio of vapor- to liquid-phase fugacities for each component must also equal unity. Figure 4 displays the final results in the vapor-phase spreadsheet. This solution required about two minutes using a Mac IIsi.



Thermodynamic Properties for Mixtures from the Peng-Robinson Equation

Enter data into outlined cells only
T = 299.8 K
P = 2.35E+00 MPa

use binary interaction parameters?
yes

Pseudocritical Properties from Kay's Rules
T'c = 315.15 K
P'c = 4.76 MPa
T'r = 0.9514
P'r = 0.4948

R = 8.31E-06 m^3 MPa/mol-K
T ref = 273.159 K
P ref = 0.001 MPa

Calculate parameters in Peng-Robinson Equation of State
am = 6.91E-07 m^6 MPa/mol^2
bm = 4.36E-05 m^3/mol
Am = 2.62E-01
Bm = 4.12E-02
dam/dT = -1.19E-09 m^6 MPa/mol^2-K
Solve Peng-Robinson EOS for Z
a1 = -9.59E-01 Q = 4.4E-02
a2 = 1.74E-01 R = -9.3E-03
a3 = -9.02E-03 Q^3-R^2 = -1.0E-06
One Real Root
Z = 0.7395

Z = 7.40E-01
f = 1.86E+00 MPa
H = #VALUE! J/mol
S = #VALUE! J/mol-K
G = #VALUE! J/mol
A = #VALUE! J/mol
U = #VALUE! J/mol
V = 7.83E-04 m^3/mol

H-Higm = -1.92E+03 J/mol
S-Sigm = -4.43E+00 J/mol-K
G-Gigm = -5.92E+02 J/mol
Higm = #VALUE! J/mol
Sigm = #VALUE! J/mol-K

Compound	**Mole Frac**	**fug. vapor (MPa)**	**fug. liquid (MPa)**	**Ratio**
C2H4	0.438	8.98E-01	8.98E-01	1.00
Butane	0.047	6.18E-02	6.18E-02	1.00
CO	0.000	0.00E+00	0.00E+00	
Ethane	0.295	5.68E-01	5.68E-01	1.00
Methane	0.000	0.00E+00	0.00E+00	
Methanol	0.000	0.00E+00	0.00E+00	
N2	0.000	0.00E+00	0.00E+00	
O2	0.000	0.00E+00	0.00E+00	
Propane	0.221	3.45E-01	3.45E-01	1.00
Water	0.000	0.00E+00	0.00E+00	
	1.000			

0

Compound	**Moles in Mixture**	**Tc (K)**	**Pc (MPa)**	**ω**	**Cpa J/mol-K**	**Cpb J/mol-K^2**	**Cpc J/mol-K^3**	**Cpd J/mol-K^4**	**b**	**κ**	**α**	**a**
C2H4	43.254	282.4	5.036	0.085					3.63E-05	0.504	0.970	4.85E-07
Butane	4.611	425.2	3.800	0.193					7.24E-05	0.662	1.224	1.84E-06
CO	0.000	133.0	3.496	0.049					2.46E-05	0.450	0.600	9.59E-08
Ethane	29.159	305.4	4.884	0.098					4.04E-05	0.523	1.010	6.09E-07
Methane	0.000	190.7	4.600	0.008					2.68E-05	0.387	0.813	2.03E-07
Methanol	0.000	513.2	7.954	0.559					4.17E-05	1.152	1.617	1.69E-06
N2	0.000	126.2	3.394	0.040					2.41E-05	0.436	0.584	8.66E-08
O2	0.000	154.4	5.046	0.021					1.98E-05	0.407	0.705	1.05E-07
Propane	21.828	369.8	4.246	0.152					5.63E-05	0.603	1.124	1.14E-06
Water	0.000	647.3	22.048	0.344					1.90E-05	0.873	1.636	9.82E-07
TOTAL	98.853				#VALUE!	#VALUE!	#VALUE!	#VALUE!				

Binary Interaction Parameters:

	C2H4	Butane	CO	Ethane	Methane	Methanol	N2	O2	Propane	Water
C2H4	0	0.092	0	0.01	0	0	0	0	0	0
Butane	0.092	0	0	0.01	0	0	0	0	0.003	0
CO	0	0	0	0	0	0	0	0	0	0
Ethane	0.01	0.01	0	0	0	0	0	0	0.001	0
Methane	0	0	0	0	0	0	0	0	0	0
Methanol	0	0	0	0	0	0	0	0	0	0
N2	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0
Propane	0	0.003	0	0.001	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0	0

Figure 4. *Spreadsheet for vapor phase of vapor-liquid equilibrium mixture used to solve Example 9.6 in Kyle.*

Another application of the mixtures spreadsheet is to link it with a spreadsheet that does chemical equilibrium calculations so that chemical equilibrium in non-ideal phases can be treated. This application is discussed in the next section.

Chemical Equilibrium

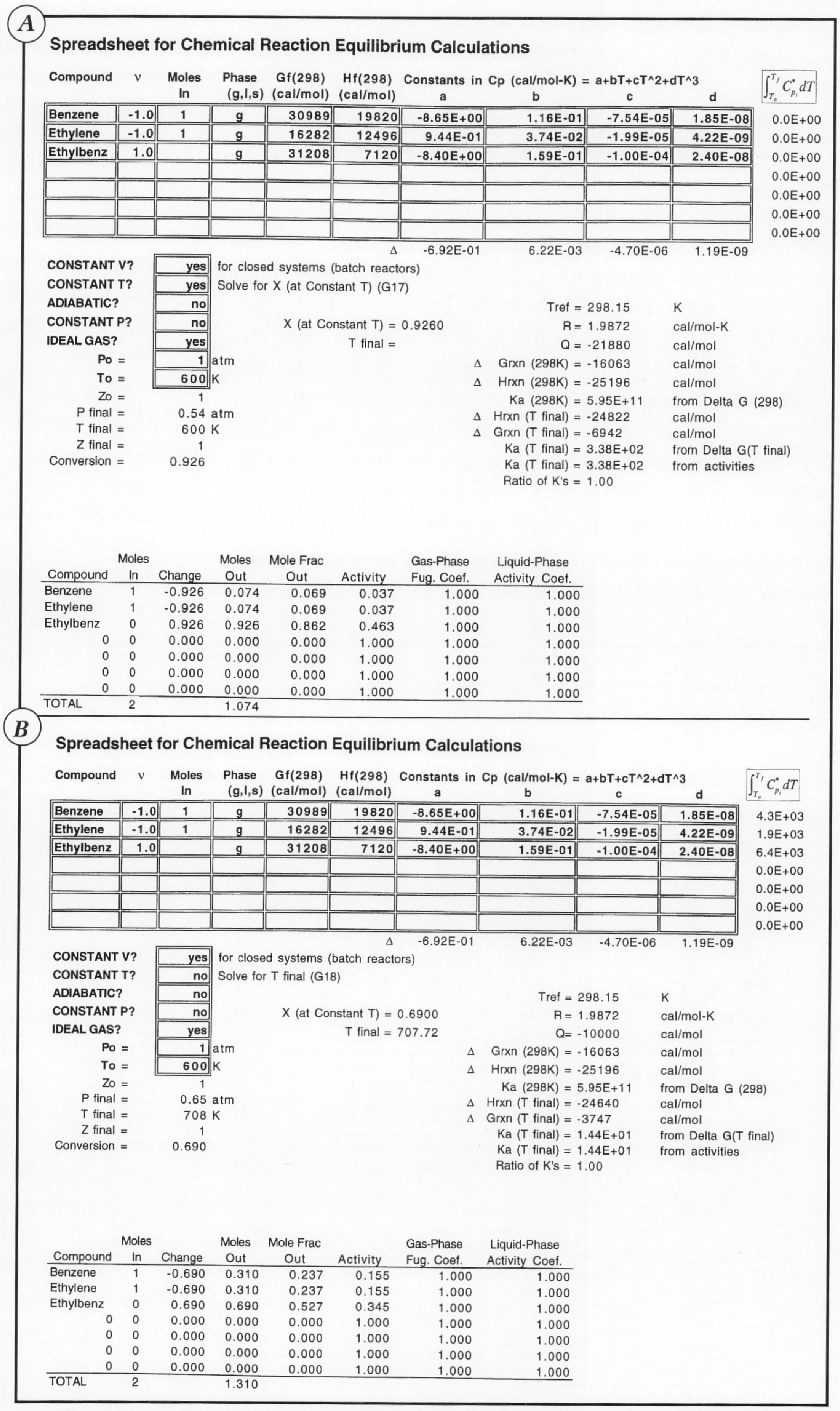
The final spreadsheet we developed performs chemical equilibrium calculations for single reactions occurring in either ideal or non-ideal fluid phases (see Figure 5, next page). The user supplies the stoichiometric coefficients (positive for products, negative for reactants), initial numbers of moles, chemical identities, standard heats and free energies of formation, and the constants in the heat capacity equation for all species involved in the reaction. Inert compounds are so indicated by using a stoichiometric coefficient of zero. The compound entered in the first row must be the limiting reactant. The user must also specify whether each component is in the gas, liquid, or solid phase, so that the activity of each component will be calculated properly. The spreadsheet can handle problems involving heterogeneous reactions. The user can also indicate whether the reaction occurs at constant volume, constant temperature, constant pressure, or adiabatically. Reactions occurring in an ideal gas phase can be so indicated. Finally, the user can specify the initial temperature and pressure of the system.

The spreadsheet uses the thermochemical data to calculate the change in free energy for the reaction and subsequently the equilibrium constant at any specified temperature. This value appears in the cell labeled $K_a(T_{final})$ from Delta $G(T_{final})$. The spreadsheet also calculates the activity of each component in the reacting mixture (including fluid-phase non-idealities), and subsequently the value of $\prod_i a_i^{\nu_i}$, which must equal the value of K_a calculated from thermodynamics when chemical equilibrium is achieved. The spreadsheet will also calculate the amount of heat transferred during the reaction. This calculation neglects any work done on or by the system, and it assumes that all components enter the system at the same temperature and that all components leave the system at the same temperature. The spreadsheet also neglects solution non-idealities (*e.g.*, we take $\underline{H}_i = \overline{H}_i$).

The types of chemical equilibrium problems typically encountered are those where temperature is known and the equilibrium composition (or conversion) and Q are sought, or those where Q is known and the equilibrium composition and temperature are sought. The spreadsheet can solve both types of problems and their variations, as shown in Figure 5.

Figure 5a gives the solution to Problem 9.24 in Sandler. The student is given a gas-phase chemical reaction (the addition of ethylene to benzene to make ethylbenzene) and told that it occurs isothermally at 600K in a constant-volume batch reactor. He is then asked to determine the equilibrium conversion and the amount of heat transferred during the reaction. This is an example of the first type of chemical equilibrium problem, wherein T is known and Q and X are sought. After the data were entered into the spreadsheet, I solved the problem by instructing the Solver to vary the conversion such that the value of K_a computed from the components' activities became equal to the equilibrium constant determined from the thermochemical data. After the conversion was determined, Q was calculated from an energy balance.

Figure 5b shows a variation of Problem 9.24, which illustrates the second type of chemical equilibrium problem.



A

Spreadsheet for Chemical Reaction Equilibrium Calculations

Compound	ν	Moles In	Phase (g,l,s)	Gf(298) (cal/mol)	Hf(298) (cal/mol)	Constants in Cp (cal/mol-K) = a+bT+cT^2+dT^3				$\int_{T_o}^{T_f} C^\circ_{p_i} dT$
						a	b	c	d	
Benzene	-1.0	1	g	30989	19820	-8.65E+00	1.16E-01	-7.54E-05	1.85E-08	0.0E+00
Ethylene	-1.0	1	g	16282	12496	9.44E-01	3.74E-02	-1.99E-05	4.22E-09	0.0E+00
Ethylbenz	1.0		g	31208	7120	-8.40E+00	1.59E-01	-1.00E-04	2.40E-08	0.0E+00
										0.0E+00
										0.0E+00
										0.0E+00
										0.0E+00
					Δ	-6.92E-01	6.22E-03	-4.70E-06	1.19E-09	

CONSTANT V? yes for closed systems (batch reactors)
CONSTANT T? yes Solve for X (at Constant T) (G17)
ADIABATIC? no
CONSTANT P? no
IDEAL GAS? yes
Po = 1 atm
To = 600 K
Zo = 1
P final = 0.54 atm
T final = 600 K
Z final = 1
Conversion = 0.926

X (at Constant T) = 0.9260
T final =

Tref = 298.15 K
R = 1.9872 cal/mol-K
Q = -21880 cal/mol
Δ Grxn (298K) = -16063 cal/mol
Δ Hrxn (298K) = -25196 cal/mol
Ka (298K) = 5.95E+11 from Delta G (298)
Δ Hrxn (T final) = -24822 cal/mol
Δ Grxn (T final) = -6942 cal/mol
Ka (T final) = 3.38E+02 from Delta G(T final)
Ka (T final) = 3.38E+02 from activities
Ratio of K's = 1.00

Compound	Moles In	Change	Moles Out	Mole Frac Out	Activity	Gas-Phase Fug. Coef.	Liquid-Phase Activity Coef.
Benzene	1	-0.926	0.074	0.069	0.037	1.000	1.000
Ethylene	1	-0.926	0.074	0.069	0.037	1.000	1.000
Ethylbenz	0	0.926	0.926	0.862	0.463	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
TOTAL	2		1.074				

B

Spreadsheet for Chemical Reaction Equilibrium Calculations

Compound	ν	Moles In	Phase (g,l,s)	Gf(298) (cal/mol)	Hf(298) (cal/mol)	Constants in Cp (cal/mol-K) = a+bT+cT^2+dT^3				$\int_{T_o}^{T_f} C^\circ_{p_i} dT$
						a	b	c	d	
Benzene	-1.0	1	g	30989	19820	-8.65E+00	1.16E-01	-7.54E-05	1.85E-08	4.3E+03
Ethylene	-1.0	1	g	16282	12496	9.44E-01	3.74E-02	-1.99E-05	4.22E-09	1.9E+03
Ethylbenz	1.0		g	31208	7120	-8.40E+00	1.59E-01	-1.00E-04	2.40E-08	6.4E+03
										0.0E+00
										0.0E+00
										0.0E+00
										0.0E+00
					Δ	-6.92E-01	6.22E-03	-4.70E-06	1.19E-09	

CONSTANT V? yes for closed systems (batch reactors)
CONSTANT T? no Solve for T final (G18)
ADIABATIC? no
CONSTANT P? no
IDEAL GAS? yes
Po = 1 atm
To = 600 K
Zo = 1
P final = 0.65 atm
T final = 708 K
Z final = 1
Conversion = 0.690

X (at Constant T) = 0.6900
T final = 707.72

Tref = 298.15 K
R = 1.9872 cal/mol-K
Q= -10000 cal/mol
Δ Grxn (298K) = -16063 cal/mol
Δ Hrxn (298K) = -25196 cal/mol
Ka (298K) = 5.95E+11 from Delta G (298)
Δ Hrxn (T final) = -24640 cal/mol
Δ Grxn (T final) = -3747 cal/mol
Ka (T final) = 1.44E+01 from Delta G(T final)
Ka (T final) = 1.44E+01 from activities
Ratio of K's = 1.00

Compound	Moles In	Change	Moles Out	Mole Frac Out	Activity	Gas-Phase Fug. Coef.	Liquid-Phase Activity Coef.
Benzene	1	-0.690	0.310	0.237	0.155	1.000	1.000
Ethylene	1	-0.690	0.310	0.237	0.155	1.000	1.000
Ethylbenz	0	0.690	0.690	0.527	0.345	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
0	0	0.000	0.000	0.000	1.000	1.000	1.000
TOTAL	2		1.310				

Figure 5. *Solution of the two common types of chemical equilibrium problems, based on Problem 9.24 in Sandler:*
a) *T given, X and Q sought,* ***b)*** *Q given, T and X sought.*

Here I assumed that the amount of heat transferred was known (-10 kcal/mol) and that the final temperature and conversion were sought. I solved this variation by instructing the Solver to vary the final temperature and conversion until the ratio of equilibrium constants was equal to unity subject to the constraint of $Q = 10{,}000$ cal/mol. Note that for an adiabatic equilibrium problem ($Q=0$), the user needs only to vary the final temperature. The spreadsheet will automatically calculate the conversion from the energy balance.

One final application of the chemical equilibrium spreadsheet we will describe is its ability to solve problems involving reactions in non-ideal fluid phases. Such problems can be solved by linking the chemical equilibrium spreadsheet with the mixtures spreadsheet described earlier. We use Sandler's Illustration 9.1-7, which considers the water-gas shift reaction and computes the equilibrium mole fractions for CO, CO_2, H_2, and H_2O at 1000K and a pressure of 500 atm, as an example. At these conditions the gas phase is slightly non-ideal. I copied the temperature, pressure, and mole fractions appearing in the chemical equilibrium spreadsheet into the mixtures spreadsheet so that fugacity coefficients could be calculated. These fugacity coefficients were then copied into the chemical equilibrium spreadsheet and used to calculate the components' activities. The balance of the solution proceeded along the lines described above. (Although space considerations prevent reproduction here of the figure displaying the final results on both the mixtures and the chemical equilibrium spreadsheets, a copy can be obtained by contacting the author.) We note too that the chemical equilibrium spreadsheet can also handle reactions in non-ideal liquid phases. Here the user can specify an activity coefficient model (*e.g.,* van Laar, Wilson, Margules) to calculate the activity coefficients for each component from a knowledge of the mixture composition.

SUMMARY AND OUTLOOK

This paper described spreadsheets for personal computers that solve chemical equilibrium problems and use cubic equations of state to calculate thermodynamics properties for pure fluids and for mixtures. These spreadsheets can be used to solve thermodynamics problems involving real fluids. As such, engineering students can work on more realistic problems, and instructors need not rely so heavily upon the ideal gas law to teach the applications of equations of state for property evaluation. These spreadsheets have been profitably employed at the University of Michigan.

With laptop and notebook computers becoming more powerful and less expensive every year, the day that students will routinely bring computers to class rather than calculators may not be far away. Consequently, computer-based methods for evaluating thermodynamics properties for real fluids may soon replace the generalized corresponding states charts that have been used for over forty years to teach students about real fluids. The spreadsheets described in this paper are consistent with this paradigm shift in thermodynamics instruction. These spreadsheets are available to other engineering educators upon request to the author.

ACKNOWLEDGMENTS

Professor Brice Carnahan introduced me to the idea of using spreadsheets for equation-of-state calculations. As a result, students in my chemical engineering thermodynamics classes were given the assignment of developing their own spreadsheets for pure component properties. Two of these students, Nobu Itoh and Douglas VanEeuwen, then did much of the subsequent development work for the mixtures and chemical equilibrium spreadsheets. This project was partially supported by the University of Michigan Center for Research on Learning and Teaching.

NOTATION

a_i	activity of component i
a	parameter in cubic EOS, constant in ideal gas heat capacity equation
b	parameter in cubic EOS, constant in ideal gas heat capacity equation
c	constant in ideal gas heat capacity equation
C_p	ideal gas heat capacity
d	constant in ideal gas heat capacity equation
f	fugacity
$\underline{G}$	Gibbs free energy
$\underline{H}$	enthalpy
P	pressure
P_c	critical pressure
R	gas constant
$\underline{S}$	entropy
T_c	critical temperature
T	temperature
$\underline{U}$	internal energy
$\underline{V}$	molar volume
Z	compressibility factor ($Z=P\underline{V}/RT$)

Greek

$\alpha(T)$	parameter in cubic EOS
υ_i	stoichiometric coefficient for component i
ω	acentric factor

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