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 ten double-spaced pages if possible 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.

AN EXERCISE FOR PRACTICING PROGRAMMING IN THE ChE CURRICULUM

Calculation of Thermodynamic Properties Using the Redlich-Kwong Equation of State

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Many students find it difficult to learn programming. One source of difficulty has to do with the complexity and relevance of the examples and exercises being used. Exercises that are simple enough for a student to write a working program in a reasonable length of time, without too much frustration, are often irrelevant to their chemical engineering studies. Consequently, they often do not see the benefit in learning programming and lose interest. More complex and realistic exercises, however, may require a long and frustrating debugging period, causing them to lose faith in their ability to make the program run and discouraging them from further programming attempts.

A good exercise to help students learn programming would be one of practical importance that can be constructed gradually in several steps. At each step, new types and more complex commands would be added to the program, but only after debugging of the previous step had been completed.

This paper presents such an exercise—one that involves analytical solution of the Redlich-Kwong equation for the compressibility factor and consequent calculation of molar volume, fugacity coefficient, isothermal enthalpy, and entropy departures. The solution is demonstrated using MATLAB,1 but other programming languages (such as C or C++) can also be used.

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Calculation of the Compressibility Factor and Derived Thermodynamic Properties
Using the Redlich-Kwong Equation of State

The two-parameter Redlich-Kwong (R-K) equation of state has an accuracy that compares well with more complicated
equations that incorporate many more constants (when applied to non-polar compounds\cite{57}). The R-K equation is a cubic
equation in the volume (or in the compressibility factor) for
which analytical solutions can be found.\cite{57} After solving
for the molar volume (or compressibility factor), several
important thermodynamic functions (such as fugacity co-
efficient, isothermal enthalpy, and entropy departures) can be
calculated.

In this exercise, the molar volume, the compressibility fac-
tor, the isothermal enthalpy departure, the isothermal entropy
departure, and the fugacity coefficients are calculated and
plotted for water vapor in the supercritical region. The val-
ues of reduced pressure and reduced temperature used are
shown in Table 1.

\textit{Equations and Numerical Data}

The R-K equation is usually written\cite{56}

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

where

\[ a = 0.42747 \left( \frac{R^2}{P_e} \right)^{5/2} \tag{2} \]

\[ b = 0.08664 \left( \frac{R_T}{P_e} \right) \tag{3} \]

and

\[ P \text{ pressure (atm)} \]

\textbf{TABLE 1}

<table>
<thead>
<tr>
<th>( P_r )</th>
<th>( P_r )</th>
<th>( P_r )</th>
<th>( P_r )</th>
<th>( T_r )</th>
<th>( T_r )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
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<td>6.2</td>
<td>8.2</td>
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<td>4.6</td>
<td>6.6</td>
<td>8.6</td>
<td>1.15</td>
</tr>
<tr>
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<td>6.8</td>
<td>8.8</td>
<td>1.2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>1.3</td>
</tr>
<tr>
<td>1.2</td>
<td>3.2</td>
<td>5.2</td>
<td>7.2</td>
<td>9.2</td>
<td>1.5</td>
</tr>
<tr>
<td>1.4</td>
<td>3.4</td>
<td>5.4</td>
<td>7.4</td>
<td>9.4</td>
<td>1.7</td>
</tr>
<tr>
<td>1.6</td>
<td>3.6</td>
<td>5.6</td>
<td>7.6</td>
<td>9.6</td>
<td>2</td>
</tr>
<tr>
<td>1.8</td>
<td>3.8</td>
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<td>9.8</td>
<td>3</td>
</tr>
</tbody>
</table>

\textit{The exercise presented here enables students to start a programming
assignment at a fairly simple level and to build it up gradually to a more complex
assignment of practical importance...}

\[ V \text{ molar volume (liters/g-mol)} \]

\[ T \text{ temperature (K)} \]

\[ R \text{ gas constant } [R = 0.08206 \text{ (atm-liter/g-mol-K)}] \]

\[ T_c \text{ critical temperature (K)} \]

\[ P_r \text{ critical pressure (atm)} \]

Eliminating \( V \) from Eq. (1) and writing it as a cubic equa-
tion of the compressibility factor, \( z \), yields

\[ f(z) = z^3 - z^2 - qz - r = 0 \tag{4} \]

where

\[ r = A^2B \tag{5} \]

\[ q = B^2 + B - A^2 \tag{6} \]

\[ A^2 = 0.42747 \left( \frac{P_r}{P_e} \right)^{5/2} \tag{7} \]

\[ B = 0.08664 \left( \frac{P_r}{P_e} \right) \tag{8} \]

in which \( P_r \) is the reduced pressure (\( P/P_c \)) and \( T_r \) is the
reduced temperature (\( T/T_c \)).

Equation (4) can be solved analytically for three roots, some
of which may be complex. Considering only the real roots,
the sequence of calculations involves the steps

\[ C = \left( \frac{f}{3} \right) + \left( \frac{g}{2} \right)^2 \tag{9} \]

where

\[ f = -3q - 1 \tag{10} \]

\[ g = 27r - 9q - 2 \tag{11} \]

If \( C > 0 \), there is one real solution for \( z \):

\[ z = D + E + 1/3 \tag{12} \]

where

\[ D = \left( -\frac{g}{2} + \sqrt{C} \right)^{1/3} \tag{13} \]

\[ E = \left( -\frac{g}{2} - \sqrt{C} \right)^{1/3} \tag{14} \]

If \( C < 0 \), there are three real solutions for \( z \):

\[ z_k = 2 \sqrt{\frac{f}{3}} \cos \left( \frac{\phi}{3} + \frac{2n(k - 1)}{3} \right) + \frac{1}{3} \quad k = 1, 2, 3 \tag{15} \]

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where

$$\phi = a \cos \left( \sqrt[4]{\frac{g^2}{4} / \frac{v}{f}} \right)$$

In the supercritical region, two of these solutions are negative, so the maximal $z_i$ is selected as the true compressibility factor.

After calculating the compressibility factor, the molar volume ($V$), the isothermal enthalpy departure ($\Delta H^*$), the isothermal entropy departure ($\Delta S^*$), and the fugacity coefficient ($\psi$) are calculated from

$$V = \frac{2RT}{P}$$

$$\Delta H^* = \frac{3a}{2bRT^{3/2}} \ln \left( \frac{1 + \frac{b}{V}}{V} \right) - (z - 1)$$

$$\Delta S^* = \frac{a}{2bRT^{3/2}} \ln \left( \frac{1 + \frac{b}{V}}{V} \right) - \ln \left( \frac{z - \frac{Pb}{RT}}{V} \right)$$

$$\psi = \exp \left( z - 1 - \ln \left( \frac{z + \frac{a}{bRT^{3/2}} \ln \left( 1 + \frac{b}{V} \right)}{V} \right) \right)$$

The numerical data needed for solving this problem include $R = 0.08206$ liter atm/g mol K, critical temperature for water $T_c = 647.4$ K, and critical pressure of water $P_c = 218.3$ atm.

**Recommended Steps for Solution**

1. Prepare a MATLAB m-file for solving the set of equations for $Tr = 1.2$ and $Pr = 5$ (C, in Eq. 9, is positive) and $Tr = 10$ and $Pr = 5$ (C, in Eq. 9, is negative). Compare the results obtained with values from generalized charts of thermodynamic properties.

2. Convert the program developed in part 1 to a function and write a main program to carry out the calculations for $Pr = 5$ and the set of $Tr$ values shown in Table 1.

3. Extend the main program to carry out the calculations for all $Pr$ and $Tr$ values shown in Table 1. Store all the results of $z$, $V$, enthalpy and entropy departures, and fugacity coefficients in column vectors. Display the various variables versus $Pr$ and $Tr$ in tabular and graphic forms.

**Solution**

The MATLAB program (m-file) for solving the set of equations for one value of $Tr$ and $Pr$ and displaying the values of selected variables is shown in Figure 1. Preparation of the program requires that students rewrite the equations using the MATLAB syntax. This stage includes changing some variable names to valid MATLAB names, changing some algebraic operators, and changing some intrinsic function names (such as converting ln to log). The use of the “max” intrinsic function to select the maximal compressibility factor from the values obtained in Eq. (15) requires storing these values in a vector.

The equations must also be reordered according to a proper computational order (thus a variable is not used before a value is assigned to it). This can be most easily achieved by first entering

R = 0.08206; % Gas constant (L atm/g mol K)
Tc = 647.4; % Critical temperature (K)
Pc = 218.3; % Critical pressure (atm)
a = 0.42747*R^2*Te^3/32/Pc; % Eq. (2), RK equation constant
b = 0.08664*R^2*Te/Pc; % Eq. (3), RK equation constant
Pr = 6; % Reduced pressure (dimensionless)
Tr = 1.2; % Reduced temperature (dimensionless)
Asqr = 0.42747*Pr/(Tr^2-2.5); % Eq. (7)
B = 0.08664*Pr/Tr; % Eq. (8)
r = Asqr*B; % Eq. (5)
g = B*2+B.Asqr; % Eq. (6)
f = (-3*q-1)*3; % Eq. (10)
g = (2-Tr^2)*q-2/27; % Eq. (11)
C = (3/3)^3+(g/2)^2; % Eq. (9)
if (C>0)
    D = ((q-2+sqrt(C))^1/3)); % Eq. (13)
    E1 = (-g-2-2*(C)); % Eq. (14)
    E = ((C-1)*E1)^1/3)); % Eq. (14)
    z = (D+E+1/3) % Compressibility factor (dimensionless)
else
    psiq = (acos(sqrt((g/2)/(-f-3/27)))); % Eq. (16)
    z1 = (2*sqrt(-f/3)*cos(psiq/3))/1+1/3; % Eq. (15)
    z2 = (2*sqrt(-f/3)*cos(psiq/3))/2+3.1416*1/3+1/3; % Eq. (15)
    z3 = (2*sqrt(-f/3)*cos(psiq/3))/2+3.1416*2/3+1/3; % Eq. (15)
    z = max(z1); % Compressibility factor (dimensionless)
end
P = Pr*Pc; % Pressure (atm)
T = Tr*Tc; % Temperature (K)
V = x*R^2/P; % Eq. (17), Molar volume (L/mol)
Hdep = (3*a*(3*a*b*R^2*Te^3/32)); % Eq. (18), Enthalpy departure (dimensionless)
Sdep = (2*a*b*R^2*Te^3/32)); % Eq. (19), Entropy departure (dimensionless)
% coeff = exp(x-1-1/3)*exp(a-b*R^2*Te^3/32)); % Eq. (20), Fugacity coefficient (dimensionless)

**Figure 1. MATLAB program for calculating compressibility factor and thermodynamic properties for one value of Re and Pr.**

**TABLE 2**

Comparison of Calculated and Generalized Chart Values for $P_r = 5$

<table>
<thead>
<tr>
<th>$Tr$</th>
<th>Calc. Value</th>
<th>Chart Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0.7326</td>
<td>0.7923</td>
</tr>
<tr>
<td>10</td>
<td>4.0706</td>
<td>4.0725</td>
</tr>
<tr>
<td>15</td>
<td>6.5006</td>
<td>6.5006</td>
</tr>
</tbody>
</table>

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the equations to a program that automatically reordered them (POLYMATH, for example). The ordered set of
equations can then be pasted into the MATLAB editor.
In addition to the "assignment" statements, this simple
program requires only the "if" statement. No commands
for printing the results are used, but selected variables
are shown during the program execution by selective addi-
tion or removal of the semicolon from the ends of the
commands. Good programming practice requires clear
descriptions of the variables and the equations by add-
ing comments.

The results obtained for compressibility factor, en-
thalpy and entropy departures, and fugacity coefficient
by the MATLAB program are compared to values of
generalized charts (Kyle20) in Table 2. The differences between
the calculated values (presumed to be more accurate) and the
generalized chart values are small enough to validate the
correctness of the MATLAB program. For
Tr = 10, no generalized chart values are
available for enthalpy and entropy depart-
ure, but the calculated values match the
trend observed in the generalized chart.

The principal change that has to be intro-
duced in the program, when proceed-
ing to the second step of the develop-
ment, includes the addition of the func-
tion definition statement

function[PT,Vz,Hdep,Sdep,f_coeff]=RKfunc(Tc,Pr,Tr,Pr);

and removal of the definition of the vari-
able Tc, Pr, Tr, and Pr. The Tr and Pr
are the parameters that are changed in the
main program. Putting the definition of Tc and Pr in the main program en-
ables easy modification of the program for different
substances. All the variables that
should be displayed in the list of
returned variables. The main program
that calls this function in order to per-
form the calculations for Pr = 5 and the
ten Tr values (shown in Table 1) is dis-
played in Figure 2.

The program starts with commands
that are not specific to the problem at
hand and fall into the category of "good
programming practice." The workspace
and the command window are cleared
and the preferred format for printing is
defined. The ten specified Tr values are
stored in a row vector Tr_list and a "for"

% A script file for calculating compressibility factor and derived
% thermodynamic properties using the Redlich Kwong equation of state.
clear, clc, format compact, format short g
Tc = 647.4; % Critical temperature (K)
Pc = 218.3; % Critical pressure (atm)
Pr = 5; % Reduced pressure (dimensionless)
Tr_list=[1 1.05 1.1 1.15 1.2 1.25 1.3 1.5 1.7 2 3];
for j=1:10
    Tr = Tr_list(j); % Reduced temperature (dimensionless)
    [P,TVz,Hdep,Sdep,f_coeff]=RKfunc(Tc,Pr,Tr,Pr);
end

Figure 2. Main program for carrying out the calculations for one
Pr and ten Tr values.

Table dimensions: 595.0x842.0
[Image 57x144 to 552x774]
[552x144]

% Print tabular results
% for i=1:10
    disp('');
    disp('Tr = num2str(Tr_list(i))' T(K) = num2str(T(Tc)*To));
    disp('');
    disp('Pr (atm) V(L/g-mol) z Hdep Sdep f_coeff');
    Res=[Pr_list(1) P(1) V(1) z(1) Hdep(1) Sdep(1) f_coeff(1)];
    disp(Res);
    pause;
end

% Plot results
% plot(Pr_list,z(1),',',Pr_list,z(2),',',Pr_list,z(3),',',Pr_list,z(4),',',Pr_list,z(5),',',...
   Pr_list,z(6),',',Pr_list,z(7),',',Pr_list,z(8),',',Pr_list,z(9),',',Pr_list,z(10),',');
legend(Tr='1',',',Tr='1.05',',',Tr='1.1',',',Tr='1.15',',',Tr='1.2',',',Tr='1.25',',',Tr='1.3',',',Tr='1.5',',',Tr='1.7',',',Tr='2',',',Tr='3');
title('Compressibility Factor Versus Tr and Pr');
xlabel('Reduced Pressure Pr');
ylabel('Compressibility Factor(z)');
pause

plot(Pr_list,f_coeff(1),',',Pr_list,f_coeff(2),',',Pr_list,f_coeff(3),',',Pr_list,f_coeff(4),',',
    Pr_list,f_coeff(5),',',Pr_list,f_coeff(6),',',Pr_list,f_coeff(7),',',Pr_list,f_coeff(8),',',
    Pr_list,f_coeff(9),',',Pr_list,f_coeff(10),');
legend(Tr='1',',',Tr='1.05',',',Tr='1.1',',',Tr='1.15',',',Tr='1.2',',',Tr='1.25',',',Tr='1.3',',',Tr='1.5',',',Tr='1.7',',',Tr='2',',',Tr='3');
title('Fugacity Coefficient Versus Tr and Pr');
xlabel('Reduced Pressure Pr');
ylabel('Fugacity Coefficient(f)');
pause

% A script file for calculating compressibility factor and derived
% thermodynamic properties using the Redlich Kwong equation of state.
clear, clc, format compact, format short g
Tc = 647.4; % Critical temperature (K)
Pc = 218.3; % Critical pressure (atm)
Pr = 5; % Reduced pressure (dimensionless)
Tr_list=[1 1.05 1.1 1.15 1.2 1.25 1.3 1.5 1.7 2 3];
for j=1:10
    Tr = Tr_list(j); % Reduced temperature (dimensionless)
    [P,TVz,Hdep,Sdep,f_coeff]=RKfunc(Tc,Pr,Tr,Pr);
end

Figure 3. Port of the main program in its final form.

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statement is used to call the function while changing the parameter values. The results are displayed in a very rudimentary form, just by omitting the semicolon after the call to the function.

After verifying that this function works properly, the assignment can be finished by adding to the main program the set of Pr values shown in Table 1, storing the results, and displaying them in tabular and graphic forms. Part of the main program in its final form is shown in Figure 3.

In this program, a “while” statement is used to input the required Pr values into the row vector Pr_list. The intrinsic function “size” is used to determine the number of elements in Pr_list. The values returned from the function are stored in two-dimensional matrices, one column for each Tr and one row for each Pr value. Tables of results are printed for a constant Tr value, where the respective columns of the results matrices are united into a single matrix, “Res” which is displayed.

Only the code for plotting the compressibility factor and the fugacity coefficient is shown, and the additional variables can be plotted similarly. The plots of the compressibility factor versus Tr and Pr and the fugacity coefficient versus Tr and Pr are shown in Figures 4 and 5, respectively. These plots are almost identical to the generalized charts that can be found in the thermodynamics textbooks.

CONCLUSION

The exercise presented here enables students to start a programming assignment at a fairly simple level and to build it up gradually to a more complex assignment of practical importance in chemical engineering. It demonstrates several aspects of good programming practice:

- The use of comments to clearly describe equations and variables
- Clearing the workspace and command window before starting execution
- Proper ordering of the equations
- Modular construction of the program, where each module is tested separately before its integration with the other components

A variety of the variable types (i.e., scalar and matrix), intrinsic functions, and simple and complex commands are used. Thus, the exercise can cover a considerable portion of a programming course.

Because of the gradual increase of difficulty in building this program, most students can successfully complete it and thus gain confidence in their ability to write a “real” program. The outcome of the exercise, the set of diagrams that for many decades has been a very important component in all thermodynamic textbooks, provides an excellent demonstration of the importance of programming in chemical engineering.

REFERENCES

1. MATLAB is a trademark of The Math Works, Inc. <http://www.mathworks.com>