

## Problem Solving with EXCEL

### 4.1 MOLAR VOLUME AND COMPRESSIBILITY FROM REDLICH-KWONG EQUATION

#### 4.1.1 Concepts Demonstrated

Analytical solution of the cubic Redlich-Kwong equation for compressibility factor and calculation of the molar volume at various reduced temperature and pressure values.

#### 4.1.2 Numerical Methods Utilized

Solution of a set of explicit equations.

#### 4.1.3 Excel Options and Functions Demonstrated

Explicit solution involving definition of constants and arithmetic formulas, arithmetic functions, creating series, absolute and relative addressing, if statements and logical functions, two-input data tables and XY (scatter) plots.

#### 4.1.4 Problem Definition

The R-K equation is usually written (Shacham et al.<sup>7</sup>)

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)\sqrt{T}} \quad (4-1)$$

where

$$a = 0.42747 \left( \frac{R^2 T_c^{5/2}}{P_c} \right) \quad (4-2)$$

$$b = 0.08664 \left( \frac{RT_c}{P_c} \right) \quad (4-3)$$

and

$P$  = pressure in atm  
 $V$  = molar volume in liters/g-mol  
 $T$  = temperature in K  
 $R$  = gas constant ( $R = 0.08206$  (atm-liter/g-mol·K))  
 $T_c$  = critical temperature in K  
 $P_c$  = critical pressure in atm

The compressibility factor is given by

$$z = \frac{PV}{RT} \quad (4-4)$$

Equation (4-1) can be written, after considerable algebra, in terms of the compressibility factor as a cubic equation (see Seader and Henley<sup>6</sup>)

$$f(z) = z^3 - z^2 - qz - r = 0 \quad (4-5)$$

where

$$r = A^2 B \quad (4-6)$$

$$q = B^2 + B - A^2 \quad (4-7)$$

$$A^2 = 0.42747 \left( \frac{P_R}{T_R^{5/2}} \right) \quad (4-8)$$

$$B = 0.086664 \left( \frac{P_R}{T_R} \right) \quad (4-9)$$

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

Equation (4-5) can be solved analytically for three roots. Some of these roots are complex. Considering only the real roots, the sequence of calculations involves the steps

$$C = \left( \frac{f}{3} \right)^3 + \left( \frac{g}{2} \right)^2 \quad (4-10)$$

where

$$f = \frac{-3q-1}{3} \quad (4-11)$$

$$g = \frac{-27r-9q-2}{27} \quad (4-12)$$

If  $C > 0$  there is one real solution for  $z$  given by

$$z = D + E + 1/3 \quad (4-13)$$

where

$$D = (-g/2 + \sqrt{C})^{1/3} \quad (4-14)$$

$$E = (-g/2 - \sqrt{C})^{1/3} \quad (4-15)$$

If  $C < 0$ , there are three real solutions

$$z_k = 2\sqrt{\frac{-f}{3}} \cos\left[\left(\frac{\phi}{3}\right) + \frac{2\pi(k-1)}{3}\right] + \frac{1}{3} \quad k = 1, 2, 3 \quad (4-16)$$

where

$$\phi = a \cos \sqrt{\frac{g^2/4}{(-f^3)/27}} \quad (4-17)$$

In the supercritical region when  $T_r \geq 10$ , two of these solutions are negative, so the maximal  $z_k$  is selected as the true compressibility factor.

- (a) Use POLYMATH to calculate the volume of steam (critical temperature is  $T_c = 647.4$  K and critical pressure is  $P_c = 218.3$  atm) at  $T_r = 1.0$  and  $P_r = 1.2$ . Compare your result with the value obtained from a physical property data base ( $V = 0.052456$  L/g-mol). Also complete the calculation for  $T_r = 3.0$  and  $P_r = 10$  ( $V = 0.0837$  L/g-mol). Carry out both calculations only if the parameter  $C > 0$ .
- (b) Calculate the compressibility factor and the molar volume of steam using Excel for the reduced temperatures and reduced pressures listed in Table 4-1. Prepare a table and a plot of the compressibility factor versus  $P_r$  and  $T_r$  as well as a table and a plot of the molar volume versus pressure and  $T_r$ . The pressure and the volume should be in a logarithmic scale in the second plot.

**Table 4-1** Reduced Pressures and Temperatures for Calculation

| $P_r$ | $P_r$ | $P_r$ | $P_r$ | $P_r$ | $T_r$ |
|-------|-------|-------|-------|-------|-------|
| 0.1   | 2     | 4     | 6     | 8     | 1     |
| 0.2   | 2.2   | 4.2   | 6.2   | 8.2   | 1.2   |
| 0.4   | 2.4   | 4.4   | 6.4   | 8.4   | 1.5   |
| 0.6   | 2.6   | 4.6   | 6.6   | 8.6   | 2.0   |
| 0.8   | 2.8   | 4.8   | 6.8   | 8.8   | 3.0   |
| 1     | 3     | 5     | 7     | 9     |       |
| 1.2   | 3.2   | 5.2   | 7.2   | 9.2   |       |
| 1.4   | 3.4   | 5.4   | 7.4   | 9.4   |       |
| 1.6   | 3.6   | 5.6   | 7.6   | 9.6   |       |
| 1.8   | 3.8   | 5.8   | 7.8   | 9.8   |       |
|       |       |       |       | 10    |       |

### 4.1.5 Solution

(a) The set of explicit equations is entered into the POLYMATH Nonlinear Equations Solver program for solution is shown in Table 4-2.

**Table 4-2** Equation Set in the POLYMATH Nonlinear Equation Solver - File P2-01A.POL

| Line | Equation, # Comment   |
|------|---|
| 1    | $R = 0.08206$ # Gas constant (L-atm/g-mol-K)  |
| 2    | $T_c = 647.4$ # Critical temperature (K)  |
| 3    | $P_c = 218.3$ # Critical pressure (atm)   |
| 4    | $a = 0.42747 * R^2 * T_c^{(5/2)} / P_c$ # Eq.(4-2), RK equation constant                          |
| 5    | $b = 0.08664 * R * T_c / P_c$ # Eq.(4-3), RK equation constant                                    |
| 6    | $P_r = 1.2$ # Reduced pressure (dimensionless)  |
| 7    | $T_r = 1$ # Reduced temperature (dimensionless)   |
| 8    | $r = A_{sqr} * B$ # Eq.(4-6)  |
| 9    | $q = B^2 + B - A_{sqr}$ # Eq.(4-7)  |
| 10   | $A_{sqr} = 0.42747 * P_r / (T_r^{2.5})$ # Eq.(4-8)  |
| 11   | $B = 0.08664 * P_r / T_r$ # Eq.(4-9)  |
| 12   | $C = (f/3)^3 + (g/2)^2$ # Eq.(4-10)   |
| 13   | $f = (-3 * q - 1) / 3$ # Eq.(4-11)  |
| 14   | $g = (-27 * r - 9 * q - 2) / 27$ # Eq.(4-12)  |
| 15   | $z =$ If $(C > 0)$ Then $(D + E + 1 / 3)$ Else $(0)$ # Eq.(4-13), Compressibility factor          |
| 16   | $D =$ If $(C > 0)$ Then $((-g / 2 + \text{sqrt}(C))^{(1 / 3)})$ Else $(0)$ # Eq.(4-14)            |
| 17   | $E1 =$ If $(C > 0)$ Then $(-g / 2 - \text{sqrt}(C))$ Else $(0)$ # Eq.(4-15)                       |
| 18   | $E =$ If $(C > 0)$ Then $((\text{sign}(E1) * (\text{abs}(E1))^{(1 / 3)}))$ Else $(0)$ # Eq.(4-15) |
| 19   | $P = P_r * P_c$ # Pressure (atm)  |
| 20   | $T = T_r * T_c$ # Temperature (K)   |
| 21   | $V = z * R * T / P$ # Molar volume (L/g-mol)  |

Note that the row numbers have been added only to help with the explanation; they are not part of the POLYMATH input. Some explanation is included in the POLYMATH input in form of optional comments (text that starts with the “#” sign and ends with the end of the line). In this particular problem the calculations can be carried out sequentially; thus all the equations are entered as explicit equations of the form:  $x =$  an expression, where  $x$  is a variable name. A variable name must start with an English letter and may contain English letters, numbers and the underscore sign “\_”. Note that no special characters, subscripts or superscripts, Greek letters, parentheses and arithmetic operators (such as +, /etc.) are allowed.

In expressions, the multiplications sign “\*” must be explicitly typed everywhere it is needed. For division the / (backslash) operator is used, for exponentiation the “^” operator and calculating square root the sqrt function are used. POLYMATH supports only the use of the round parentheses “()”. It is important to use enough pairs of parentheses, especially when division is involved, to obtain the correct sequence of calculations.

The equations can be entered into POLYMATH in any order as POLYMATH reorders the equations so that variables are calculated, appearing on the left hand side of the equal sign, before they appear in an expression on the right

hand side of the equal sign. In the set of equations given in Table 4-2 for example, POLYMATH will first calculate f in line 13 and then g in line 14 before calculating C in line 12.

The calculation of the compressibility factor for the case where  $C > 0$  is carried out by the equations in lines 15-18 in Table 4-2. Calculations with variables E 1 and E in lines 17 and 18 deal with possible negative cube roots. Note that the POLYMATH if statement ensures that the variables are calculated if  $C > 0$ , otherwise zero value is substituted for them. The syntax of the if statement is:

x = if (condition) then (expression 1) else (expression 2)

The condition may include the following operators: and, or (Boolean operators), >, <, >=, <=, == (equals). The expressions may be any formula, including another 'if' statement. Note that Equations (4-16) and (4-17) for calculating the compressibility factor if  $C < 0$  are not included in the equation set of Table 4-2.

The POLYMATH solution obtained for  $T_r = 1.0$  and  $P_r = 1.2$  is  $V = 0.052298$  L/g-mol; this is about 0.2% different from the value from the physical property data base. The compressibility factor at this point is:  $z = 0.25788$ . At  $T_r = 3.0$  and  $P_r = 10$  the POLYMATH solutions obtained are  $V = 0.083655$  L/g-mol (the same as the given value) and  $z = 1.14586$ .

(b) The POLYMATH equation set can be exported to Excel by opening an Excel workbook, entering the POLYMATH equation editor window, and pressing the Excel icon or F4 key. The Excel Worksheet that is automatically generated is partially shown in Figure 4-1. Column "A" indicates the type of the equations (all "Explicit" in this particular case). Column "B" shows the variable names, as defined in the POLYMATH file while column "C" gives their numerical values. Column "D" actually contains the Excel formulas for calculating the variable val-

|    | A                                      | B               | C            | D | E  | F                                  |
|----|--|-----------------|--------------|---|--|------------------------------------|
| 1  | <b>POLYMATH NLE Migration Document</b> |                 |              |   |  |                                    |
| 2  |  | <b>Variable</b> | <b>Value</b> |   | <b>Polymath Equation</b>                                 | <b>Comments</b>                    |
| 3  | Explicit Eqs                           | R               | 0.08206      |   | $R=0.08206$  | Gas constant (L-atm/g-mol-K)       |
| 4  |  | Tc              | 647.4        |   | $Tc=647.4$   | Critical temperature (K)           |
| 5  |  | Pc              | 218.3        |   | $Pc=218.3$   | Critical pressure (atm)            |
| 6  |  | a               | 140.619862   |   | $a=0.42747 * R^2 * Tc^{(5/2)} / Pc$                      | Eq. (4-2), RK equation constant    |
| 7  |  | b               | 0.02108477   |   | $b=0.08664 * R * Tc / Pc$                                | Eq. (4-3), RK equation constant    |
| 8  |  | Pr              | 1.2          |   | $Pr=0.1$   | Reduced pressure (dim)             |
| 9  |  | Tr              | 1            |   | $Tr=1$   | Reduced temperature (dim)          |
| 10 |  | r               | 0.05333184   |   | $r=Asqr * B$   | Eq. (4-6)                          |
| 11 |  | q               | -0.3981867   |   | $q=B^2 + B - Asqr$                                       | Eq. (4-7)                          |
| 12 |  | Asqr            | 0.512964     |   | $Asqr=0.42747 * Pr / (Tr^{2.5})$                         | Eq. (4-8)                          |
| 13 |  | B               | 0.103968     |   | $B=0.08664 * Pr / Tr$                                    | Eq. (4-9)                          |
| 14 |  | C               | 1.7186E-05   |   | $C=(f/3)^3 + (g/2)^2$                                    | Eq. (4-10)                         |
| 15 |  | f               | 0.06485332   |   | $f=(-3 * q - 1) / 3$                                     | Eq. (4-11)                         |
| 16 |  | g               | 0.00532297   |   | $g=(-27 * r - 9 * q - 2) / 27$                           | Eq. (4-12)                         |
| 17 |  | z               | 0.25788001   |   | $z=if(C > 0) Then (D + E + 1/3) Else (0)$                | Eq. (4-13), Compressibility factor |
| 18 |  | D               | 0.11406621   |   | $D=if(C > 0) Then ((-g/2 + sqrt(C))^(1/3)) Else (0)$     | Eq. (4-14)                         |
| 19 |  | E1              | -0.0068071   |   | $E1=if(C > 0) Then (-g/2 - sqrt(C)) Else (0)$            | Eq. (4-15)                         |
| 20 |  | E               | -0.1895195   |   | $E=if(C > 0) Then ((sign(E1) * abs(E1))^(1/3)) Else (0)$ | Eq. (4-15)                         |
| 21 |  | P               | 261.96       |   | $P=Pr * Pc$  | Pressure (atm)                     |
| 22 |  | T               | 647.4        |   | $T=Tr * Tc$  | Temperature (K)                    |
| 23 |  | V               | 0.05229822   |   | $V=z * R * T / P$  | Molar volume (L/g-mol)             |

Figure 4-1 POLYMATH Equation Set Exported to Excel - File P4-01B1.XLS

|   | A            | B        | C  | D | E                                       | F                   |
|---|--------------|----------|--|---|---|---------------------|
| 2 |              | Variable | Value  |   | Polymath Equation                       | Comments            |
| 3 | Explicit Eqs | R        | =0.08206   |   | $R=0.08206$                             | Gas constant (L-a   |
| 4 |              | Tc       | =647.4   |   | $Tc=647.4$                              | Critical temperatur |
| 5 |              | Pc       | =218.3   |   | $Pc=218.3$                              | Critical pressure ( |
| 6 |              | a        | =(((0.42747 * (C3 ^ 2)) * (C4 ^ (5 / 2)))) / C5) |   | $a=0.42747 * R ^ 2 * Tc ^ (5 / 2) / Pc$ | Eq. (4-2), RK equa  |
| 7 |              | b        | =(((0.08664 * C3) * C4) / C5)                    |   | $b=0.08664 * R * Tc / Pc$               | Eq. (4-3), RK equa  |

Figure 4-2 Some of the Excel Formulas of the Exported Problem - File P4-01B1.XLS

ues but these formulas can be seen only when pointing on a particular cell or when selecting the “View Formulas” option from the Excel “Tools/Options/View” dropdown menu.

Columns “E” and “F” present the POLYMATH equations and comments (not completely shown) for documentation purposes. It is important to remember that only the Excel formulas, stored in column “C”, are used for calculations.

Some of the Excel formulas generated are shown in Figure 4-2. Several points are worth noting regarding these formulas: 1) Only the right hand side of the equations is included in the Excel formula. The value obtained is assigned to the particular cell where the formula resides (it is not assigned to a particular variable). 2) When the formula contains an expression, it must start with the equal (=) sign. If it contains only a numerical constant (like the value 0.08206), the omission of the equal sign is permitted. 3) The Excel formulas are very similar to the POLYMATH equations except that the variable names are replaced by the addresses of the cells where the particular variables are being calculated. 4) The Excel “If” statement is different from the POLYMATH “If” statement. The calculation of the compressibility factor given by  $z$  in cell C17 is carried out, for example, by the formula

$$=IF((C14 > 0), ((C18 + C20) + (1 / 3)), 0)$$

The molar volume and compressibility factor obtained by the Excel formulas for  $T_r = 1.0$  and  $P_r = 1.2$  are the same as obtained by POLYMATH (see Table 4-2); thus the correctness of the formulas has been verified. Now the calculations can be carried out for all the  $T_r$  and  $P_r$  values shown in Table 4-1. This is accomplished by the “Two Input Data Table” tool of Excel.

First the framework of the Excel Table is prepared as shown in Figure 4-3 by entering the desired  $P_r$  values listed into separate rows in column G (only

|   | G   | H                          | I      | J      | K      | L      |
|---|-----|----------------------------|--------|--------|--------|--------|
| 1 |     | Compressibility Factor (z) |        |        |        |        |
| 2 |     | Tr=1                       | Tr=1.2 | Tr=1.5 | Tr=2.0 | Tr=3.0 |
| 3 |     | 1                          | 1.2    | 1.5    | 2      | 3      |
| 4 | 0.1 |                            |        |        |        |        |
| 5 | 0.2 |                            |        |        |        |        |
| 6 | 0.4 |                            |        |        |        |        |
| 7 | 0.6 |                            |        |        |        |        |
| 8 | 0.8 |                            |        |        |        |        |
| 9 | 1   |                            |        |        |        |        |

Figure 4-3 Preparation of a “Two Input Data Table” for Calculating Compressibility Factor Values - File P4-01B1.XLS

|    | G       | H                          | I      | J      | K      | L      | M |
|----|---------|----------------------------|--------|--------|--------|--------|---|
| 1  |         | Compressibility Factor (z) |        |        |        |        |   |
| 2  |         | Tr=1                       | Tr=1.2 | Tr=1.5 | Tr=2.0 | Tr=3.0 |   |
| 3  | 0.25788 | 1                          | 1.2    | 1.5    | 2      | 3      |   |
| 4  | 0.1     |                            |        |        |        |        |   |
| 5  | 0.2     |                            |        |        |        |        |   |
| 6  | 0.4     |                            |        |        |        |        |   |
| 7  | 0.6     |                            |        |        |        |        |   |
| 8  | 0.8     |                            |        |        |        |        |   |
| 9  | 1       |                            |        |        |        |        |   |
| 10 | 1.2     |                            |        |        |        |        |   |
| 11 | 1.4     |                            |        |        |        |        |   |
| 12 | 1.6     |                            |        |        |        |        |   |
| 13 | 1.8     |                            |        |        |        |        |   |

**Figure 4-4** Selection of Row and Column Input Cells for the Excel Data Table - File **P4-01B 1.XLS**

part of the values are shown) and the  $T_r$  values are entered into separate columns in the 3rd row. The address of the calculated value of the compressibility factor (C17, see Figure 4-1) could be entered in the upper corner on the left side of the table (cell H3). Since the compressibility factor should be calculated only if the variable  $C > 0$ , the cell content should be modified to display only meaningful values. This is achieved with an "If" statement in cell H3.

$$=IF(C17>0,C17,"Irrelevant")$$

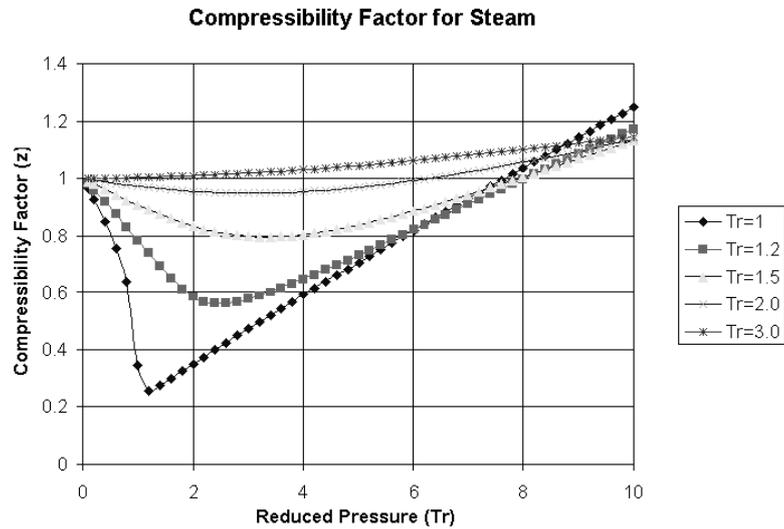
Note that the headings entered in the row 2 are not essential parts of the table, but they are used for "Legend" in the graph to be prepared.

After entering the  $P_r$  and  $T_r$  values and the address of the target result, the entire area of the table is selected and the Excel Table option from the Data menu is chosen, as shown in Figure 4-4. The address of the parameter  $T_r$  (C9, see Figure 4-1) is specified as the Row Input Cell, since the  $T_r$  values are entered in a row, and the address of the parameter  $P_r$  (C8) is specified as the Column Input Cell.

After clicking on the OK button, the Excel Table is filled with the compressibility factors corresponding to the desired reduced temperatures and reduced pressures. Partial results of the calculations are shown in Figure 4-5.

|   | G       | H                          | I        | J        | K        | L        |
|---|---------|----------------------------|----------|----------|----------|----------|
| 1 |         | Compressibility Factor (z) |          |          |          |          |
| 2 |         | Tr=1                       | Tr=1.2   | Tr=1.5   | Tr=2.0   | Tr=3.0   |
| 3 | 0.25788 | 1                          | 1.2      | 1.5      | 2        | 3        |
| 4 | 0.1     | 0.965162                   | 0.979972 | 0.990293 | 0.996817 | 1.000162 |
| 5 | 0.2     | 0.928637                   | 0.959637 | 0.980652 | 0.993718 | 1.000366 |
| 6 | 0.4     | 0.849068                   | 0.918005 | 0.961605 | 0.987783 | 1.000842 |
| 7 | 0.6     | 0.756568                   | 0.875036 | 0.942949 | 0.982211 | 1.001457 |
| 8 | 0.8     | 0.638741                   | 0.830724 | 0.924788 | 0.97702  | 1.002201 |
| 9 | 1       | 0.346664                   | 0.785203 | 0.907245 | 0.972226 | 1.003072 |

**Figure 4-5** Partial Results for Compressibility Factor Calculation for various  $P_r$  and  $T_r$  - File **P4-01B 1.XLS**



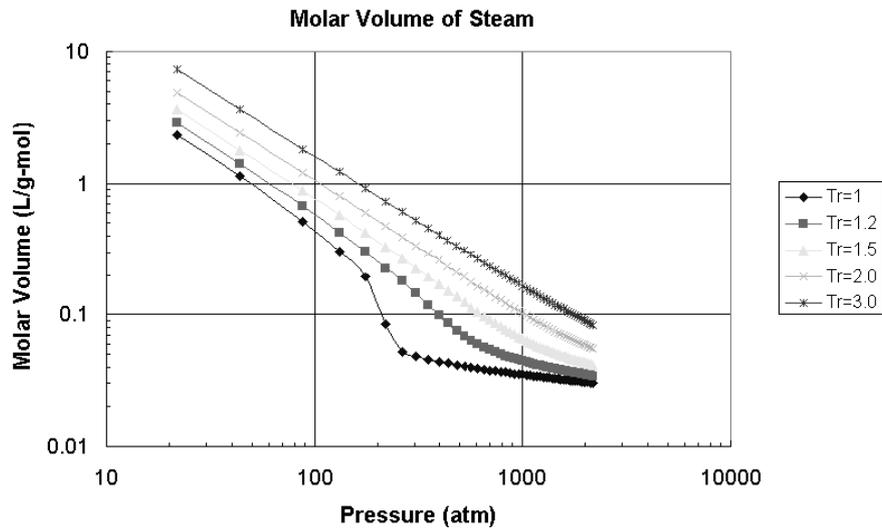
**Figure 4-6** Compressibility Factor of Steam versus  $P_r$  and  $T_r$  - File **P4-01B1.XLS**

The generated table in the Excel worksheet can be used for preparing the plot (of type: XY, scatter) of the compressibility factor  $z$  (on the Y axis) versus  $P_r$  (on the X axis) and  $T_r$  (parameter). Figure 4-6 shows the resulting Excel plot.

The molar volume at various  $P_r$  and  $T_r$  values can be calculated by generating a two input data table similar to the one shown in Figure 4-5. In this case, the address of the calculated value of the molar volume (C23, see Figure 4-1) is entered in the upper corner on the left side of the table. After the table is generated a new column containing the pressure values is added to the left of the column which contains the  $P_r$  values, as shown in Table 4-7. This table can be used for preparing the plot (of type: XY, scatter) of the molar volume (on the Y axis) versus P (on the X axis) and  $T_r$  (parameter). After the plot is prepared the “Format axis” options for both the X and Y axes have to be used to change the scales to logarithmic. The resultant plot is shown in Figure 4-8

|   | G      | H        | I        | J        | K        | L        | M        |
|---|--------|----------|----------|----------|----------|----------|----------|
| 2 | P      | Pr       | Tr=1     | Tr=1.2   | Tr=1.5   | Tr=2.0   | Tr=3.0   |
| 3 |        | 0.052298 | 1        | 1.2      | 1.5      | 2        | 3        |
| 4 | 21.83  | 0.1      | 2.348825 | 2.861839 | 3.614977 | 4.851721 | 7.302004 |
| 5 | 43.66  | 0.2      | 1.129969 | 1.401228 | 1.789891 | 2.418319 | 3.651712 |
| 6 | 87.32  | 0.4      | 0.516574 | 0.670219 | 0.877563 | 1.201937 | 1.826743 |
| 7 | 130.98 | 0.6      | 0.306865 | 0.425899 | 0.573692 | 0.796772 | 1.218577 |
| 8 | 174.64 | 0.8      | 0.194306 | 0.303248 | 0.421982 | 0.594421 | 0.914611 |
| 9 | 218.3  | 1        | 0.081361 | 0.200305 | 0.331187 | 0.473703 | 0.733725 |

**Figure 4-7** Two Input Table for Molar Volume - File **P4-01B2.XLS**



**Figure 4-8** Molar Volume of Steam versus  $P_r$  and  $T_r$  - File **P4-01B2.XLS**



The problem solution files are found in directory CHAPTER 4 and designated **P4-01A.POL**, **P4-01B 1.XLS** and **P4-01B2.XLS**