

# Efficiently Solve Complex Calculations

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Reduce the chances of computational errors by following this technique, which combines the use of a standard spreadsheet with a numerical software package.

**S**PREADSHEETS ARE COMPUTATIONAL tools that are used in the chemical industry for a wide variety of tasks. Combining spreadsheets with additional software packages can considerably speed up and increase the robustness of the spreadsheet model development (1).

Currently, spreadsheets are being used for numerical problem solving in such tasks as: solving complex equations of state for the compressibility factor with consequent calculations of various thermodynamic properties; ideal and non-ideal flash calculations; chemical equilibrium calculations; and chemical reactor design. Such calculations can be classified as systems of nonlinear algebraic equations (NLE), systems of ordinary or partial differential equations (ODE and PDE), and multiple linear, polynomial and multiple non-linear regressions.

While spreadsheets can be used for solving all of these types of problems, the time that must be invested in the technical details of the solution is often much more than that required when dedicated software packages are used. Also, the program documentation is often unsatisfactory (2). Program preparation can be accelerated considerably and the documentation of the spreadsheet version of the model and solution can be significantly improved by using the solution obtained by a numerical software package as the starting point and reference for the spreadsheet program. In this article, Microsoft Excel and the POLYMATH numerical software package (copyrighted by M. Shacham, M. B. Cutlip and M. Elly; [www.polymath-software.com](http://www.polymath-software.com)) will

be used to demonstrate this approach. The method can be applied to other spreadsheets and/or numerical software packages.

The application of this technique to complex consecutive calculations (involving several *if* conditions) will be described. For demonstration, an example is given where the analytical solution of the Redlich-Kwong (R-K) equation for the compressibility factor is used to calculate the molar volume, isothermal enthalpy and entropy departure, and fugacity coefficient.

## Converting POLYMATH files to Excel

To obtain a basic solution of a system containing several explicit algebraic equations with Excel, the equations are first entered into the POLYMATH program; subsequently, a solution is obtained and its correctness is verified. The set of equations can then be converted into an Excel worksheet in the following steps:

1. Copy the ordered explicit equations from the POLYMATH solution report.
2. Paste the equations into an Excel worksheet; remove the equation numbers.
3. Rearrange the equations in this order — constant definitions, functions of the constants, parameter definitions and explicit functions of the parameters.
4. Copy the right-hand side of the equations into the adjacent cells and replace the variable names by variable addresses. To ensure error-free variable name replacement, use the “pointing” option and click on the

cell whose address should be entered after marking the original variable name. Note that *if* statements and some functions may require additional rewriting and/or rearrangement. Use absolute addressing for the constants (and functions of constants) and relative addressing for the parameters (and functions of the parameters). Note that pressing F4 converts selected reference from relative to absolute.

5. Check the numerical value obtained in a particular cell by comparison to the POLYMATH solution.

After the correct solution for one set of parameters is obtained, the set of equations can be copied as many times as needed, or the "Table" option can be used to obtain solutions for additional parameter sets. The use of this procedure is demonstrated in the following example — calculating the compressibility factor and derived thermodynamic properties using the R-K equation of state.

The R-K equation of state has an accuracy that compares very well with equations containing many more constants when applied to non-polar compounds (3). It is a cubic equation in the volume (or in the compressibility factor) for which analytical solutions can be found (4). After solving for the molar volume (or compressibility factor), several important thermodynamic functions, such as isothermal enthalpy and entropy departures and fugacity coefficient can be calculated.

In this example the molar volume, the compressibility factor, the isothermal enthalpy departure, the isothermal entropy departure and the fugacity coefficient are calculated and plotted for water vapor in the supercritical region. The values of reduced pressure and reduced temperature used are shown in Table 1.

The R-K equation is usually written as (5):

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

where

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

$$b = 0.8664 \left( \frac{RT_c}{P_c} \right) \quad (3)$$

$P$  = pressure in atm,  $V$  = molar volume in L/g-mol,  $T$  = temperature in K,  $R$  = gas constant = 0.08206 atm·L/g-mol·K,  $T_c$  = critical temperature in K, and  $P_c$  = critical pressure in atm.

Eliminating  $V$  from Eq. 1 and writing it as a cubic equation of the compressibility factor  $z$ , yields

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

where

$$r = A^2 B \quad (5)$$

**Table 1. Reduced pressure ( $P_r$ ) and reduced temperature ( $T_r$ ) values for example problem.**

$P_r$	$P_r$	$P_r$	$P_r$	$P_r$	$T_r$
0.1	2.0	4.0	6.0	8.0	1.0
0.2	2.2	4.2	6.2	8.2	1.05
0.4	2.4	4.4	6.4	8.4	1.1
0.6	2.6	4.6	6.6	8.6	1.15
0.8	2.8	4.8	6.8	8.8	1.2
1.0	3.0	5.0	7.0	9.0	1.3
1.2	3.2	5.2	7.2	9.2	1.5
1.4	3.4	5.4	7.4	9.4	1.7
1.6	3.6	5.6	7.6	9.6	2.0
1.8	3.8	5.8	7.8	9.8	3.0

$$Q = B^2 + B - A^2 \quad (6)$$

$$A^2 = 0.42747 \left( \frac{P_r}{T_r^{5/2}} \right) \quad (7)$$

$$B = 0.8664 \left( \frac{P_r}{T_r} \right) \quad (8)$$

$P_r$  = reduced pressure ( $P/P_c$ ) and  $T_r$  = reduced temperature ( $T/T_c$ ).

Eq. 4 can be solved analytically for three roots. Some of these roots are complex. Considering only the real roots, the sequence of calculations involves the following steps:

$$C = \left( \frac{f}{3} \right)^3 + \left( \frac{g}{2} \right)^2 \quad (9)$$

where

$$f = \frac{-3q-1}{3} \quad (10)$$

$$g = \frac{-27r-9q-2}{27} \quad (11)$$

If  $C > 0$ , there is one real solution for  $z$ :

$$z = D + E + 1/3 \quad (12)$$

where

$$D = (-g/2 + \sqrt{C})^{1/3} \quad (13)$$

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

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

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

where

$$\phi = a \cos \sqrt{\frac{g^2 / 4}{-f^3 / 27}} \quad (16)$$

In the supercritical region, two of these solutions are negative, so the maximal  $z_k$  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 the following equations (5):

$$V = \frac{zRT}{P} \quad (17)$$

$$\frac{\Delta H^*}{RT} = \frac{3a}{2bRT^{3/2}} \ln\left(1 + \frac{b}{V}\right) - (z-1) \quad (18)$$

$$\frac{\Delta S^*}{R} = \frac{a}{2bRT^{3/2}} \ln\left(1 + \frac{b}{V}\right) - \ln\left(z - \frac{Pb}{RT}\right) \quad (19)$$

$$\Psi = \exp\left\{z - 1 - \ln\left[z\left(1 - \frac{b}{V}\right)\right] - \frac{a}{2bRT^{3/2}} \ln\left(1 + \frac{b}{V}\right)\right\} \quad (20)$$

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

### Equation and data input

This problem does not require iterative calculations, but because of the large number of equations and variables, direct input of the equations into Excel can be a tedious and error-prone process. A better approach is to first enter the equations into POLYMATH, which requires minimal changes in the naming of the variables, solve the equations for a few sets of parameter values and check the results. After completing this part, the conversion to Excel formulas can be carried out faster and with less probability for technical errors. The equations, as entered into the POLYMATH program, are shown in Figure 1.

The POLYMATH results for one set of values of  $T_r$  and  $P_r$  are shown in Table 2. These results were compared with generalized figures for the particular properties and con-

**Table 2. POLYMATH results for example problem, where  $T_r = 1.2$  and  $P_r = 6$ .**

Variable	Value	Variable	Value
R	0.08206	E1	-0.02402
Tc	647.4	D	0.776074
Pc	218.3	E	-0.28852
a	140.6199	z0	0.820887
b	0.021085	psii	0
Pr	6	z1	0
Tr	1.2	z2	0
Asqr	1.625937	z3	0
B	0.4332	z	0.820887
r	0.704356	P	1309.8
q	-1.00508	T	776.88
g	-0.44341	V	0.039954
f	0.671742	Hdep	2.564973
C	0.060379	Sdep	1.742845
		f_coeff	0.439495

firmed to be close to the published values (5). For the case shown,  $C > 0$ , Eqs. 15 and 16 are irrelevant, and POLYMATH sets the values of the variables calculated by these equations at zero. A different set of  $T_r$  and  $P_r$  values ( $T_r = 10$  and  $P_r = 10$ , for example) should be used to check the equations pertinent to the case of  $C < 0$ .

After the correctness of the POLYMATH equation set has been verified, proceed with the conversion of the equations to Excel formulas, as previously described. This is demonstrated in Figure 2 on a small subset of the equations. Do not name the cells in the formulas' column — doing so may cause confusion between names and addresses that may result when naming variables by short names

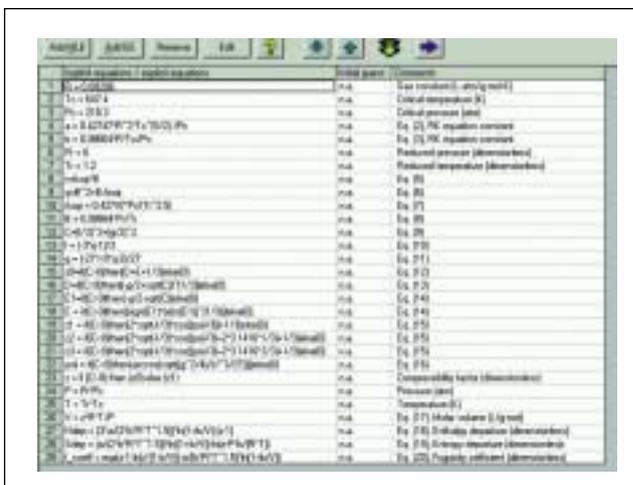


Figure 1. POLYMATH equation entry for example problem.

**Table 3. Excel formulas for example problem.**

A	B	C
Constants	R = 0.08206 Tc = 647.4 Pc = 218.3	0.08206 647.4 218.3
Functions of the constants	a = 0.42747*R^2*Tc^(5/2)/Pc b = 0.08664*R*Tc/Pc	= 0.42747*\$C\$6^2*\$C\$7^(5/2)/\$C\$8 = 0.08664*\$C\$6*\$C\$7/\$C\$8
Parameters	Tr = 1.2 Pr = 6	1.2 6
Equations	Asqr = 0.42747*Pr/(Tr^2.5) B = 0.08664*Pr/Tr q = B^2+B-Asqr r = Asqr*B f = (-3*q-1)/3 g = (-27*r-9*q-2)/27 C = (f/3)^3+(g/2)^2 D = if(C>0)then((-g/2+sqrt(C))^(1/3))else(0)  E1 = if(C>0)then(-g/2-sqrt(C))else(0) psii = if(C<0)then(arccos(sqrt((g^2/4)/(-f^3/27))))else(0)  E = if(C>0)then((sign(E1)*(abs(E1))^(1/3)))else(0)  z1 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3))+1/3)else(0)  z2 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3)+2*3.1416*1/3)+1/3)else(0) z3 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3)+2*3.1416*2/3)+1/3)else(0) z0 = if(C>0)then(D+E+1/3)else(0) z = if (C>0) then (z0) else max(z1,z2,z3) T = Tr*Tc P = Pr*Pc V=z*R*T/P Hdep = (3*a/(2*b*R*T^1.5))*ln(1+b/V)-(z-1)  Sdep = (a/(2*b*R*T^1.5))*ln((1+b/V))-ln(z-P*b/(R*T))  f_coeff = exp(z-1-ln(z*(1-b/V))-a/(b*R*T^1.5)*ln(1+b/V))	= 0.42747*C12/(C11^2.5) = 0.08664*C12/C11 = C14^2+C14-C13 = C13*C14 = (-3*C15-1)/3 = (-27*C16-9*C15-2)/27 = (C17/3)^3+(C18/2)^2 = IF(C19>0,(-C18/2+SQRT(C19))^(1/3), "IRRELEVANT") = IF(C19>0,(-C18/2-SQRT(C19)),"IRRELEVANT") = IF(C19<0,(ACOS(SQRT((C18^2/4)/(-C17^3/27))))," "IRRELEVANT") = IF(C19>0,((SIGN(C21)*(ABS(C21))^(1/3))), "IRRELEVANT") = IF(C19<0,(2*SQRT(-C17/3)*COS((C22/3))+1/3), "IRRELEVANT") = IF(C19<0,(2*SQRT(-C17/3)*COS((C22/3)+ PI()*2/3)+1/3),"IRRELEVANT") = IF(C19<0,(2*SQRT(-C17/3)*COS((C22/3)+ 2*PI()*2/3)+1/3),"IRRELEVANT") = IF(C19>0,(C20+C23+1/3),"IRRELEVANT") = IF(C19>0,C27,MAX(C24,C25,C26)) = C11*\$C\$7 = C12*\$C\$8 = C28*0.08206*C29/C30 = (3*\$C\$9/(2*\$C\$10*\$C\$6*C29^1.5))* LN(1+\$C\$10/C31)-(C28-1) = (\$C\$9/(2*\$C\$10*\$C\$6*C29^1.5))*LN((1+\$C\$10/C31)) -LN(C28-IC30*\$C\$10/(\$C\$6*C29)) = EXP(C28-1-LN(C28*(1-\$C\$10/C31))- \$C\$9/ (\$C\$10*\$C\$6*C29^1.5)*LN(1+\$C\$10/C31))

(e.g., z1, z2 and z3). Cell names are also carried over to different worksheets in the same workbook, and this can be a source of many errors. The use of absolute addressing is recommended for constants and functions of constants,

whereas relative addressing is acceptable for parameters and the functions of the parameters.

Once the Excel formula for a particular equation is complete, its numerical value is displayed. Comparing the nu-

**Table 4. Excel results for example problem with one set of  $T_r$  and  $P_r$  values.**

		Formulas	Description	Units
Constants	R = 0.08206	0.08206	Gas constant	L-atm/g-mol-K
	Tc = 647.4	647.4	Critical temperature	K
	Pc = 218.3	218.3	Critical pressure	atm
Functions of the constants	a = 0.42747*R^2*Tc^(5/2)/Pc	140.62	R-K equation constant (Eq. 2)	
	b = 0.08664*R*Tc/Pc	0.02108	R-K equation constant (Eq. 3)	
Parameters	Tr = 1.2	1.2	Reduced temperature	dimensionless
	Pr = 6	6	Reduced pressure	dimensionless
Equations	Asqr = 0.42747*Pr/(Tr^2.5)	1.62594	Eq. 7	
	B = 0.08664*Pr/Tr	0.43320	Eq. 8	
	q = B^2+B-Asqr	-1.00507	Eq. 6	
	r = Asqr*B	0.70436	Eq. 5	
	f = (-3*q-1)/3	0.67174	Eq. 10	
	g = (-27*r-9*q-2)/27	-0.44341	Eq. 11	
	C = (f/3)^3+(g/2)^2	0.06038	Eq. 9	
	D = if(C>0)then((-g/2+sqrt(C))^(1/3))else(0)	0.77607	Eq. 13	
	E1 = if(C>0)then(-g/2-sqrt(C))else(0)	-0.02402	Eq. 14	
	psii = if(C<0)then(arccos(sqrt((g^2/4)/(-f^3/27))))else(0)	IRRELEVANT	Eq. 16	
	E = if(C>0)then((sign(E1)*(abs(E1))^(1/3)))else(0)	-0.28852	Eq. 14	
	z1 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3)+1/3))else(0)	IRRELEVANT	Eq. 15	
	z2 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3)+2*3.1416*1/3)+1/3)else(0)	IRRELEVANT	Eq. 15	
	z3 = if(C<0)then(2*sqrt(-f/3)*cos((psii/3)+2*3.1416*2/3)+1/3)else(0)	IRRELEVANT	Eq. 15	
	z0 = if(C>0)then(D+E+1/3)else(0)	0.82089	Eq. 12	
	z = if (C>0)then(z0)elsemax(z1,z2,z3)	0.82089	Compressibility factor	dimensionless
	T = Tr*Tc	776.88	Temperature	K
	P = Pr*Pc	1309.80	Pressure	atm
	V = z*R*T/P	0.03995	Molar volume (Eq. 17)	L/g-mol
	Hdep = (3*a/(2*b*R*T^1.5))*ln(1+b/V)-(z-1)	2.56497	Enthalpy departure (Eq. 18)	dimensionless
Sdep = (a/(2*b*R*T^1.5))*ln((1+b/V)-ln(z*(1-b/V))-a/(b*R*T^1.5)*ln(1+b/V))	1.74284	Entropy departure (Eq. 19)	dimensionless	
f_coeff = exp(z-1-ln(z*(1-b/V))-a/(b*R*T^1.5)*ln(1+b/V))	0.43950	Fugacity coefficient (Eq. 20)	dimensionless	

merical value with the POLYMATH solution enables one to correct the mistakes immediately, saving the time wasted on debugging when the errors have already been propagated.

In addition to changing the variable names to addresses some intrinsic function names must also be changed. In this particular example the function name “arccos” used by POLYMATH must be replaced by ACOS. The syntax of the *if* statements is different in POLYMATH and Excel, so those statements must be revised accordingly.

The Excel formulas are shown in Table 3. The POLYMATH equations in column B provide complete documentation for the Excel formulas entered in column C. The nu-

merical results (Table 4) are identical to those obtained by POLYMATH. Thus the correctness of the Excel formulas has been verified.

Once a well-documented and verified Excel solution for one set of parameter values is available, one can proceed to the preparation of the required tables and graphs of the compressibility factor and the thermodynamic properties as functions of  $T_r$  and  $P_r$ . The tables can be very conveniently prepared using the “Two-Input Data Table” option of Excel. The preparation of such a table for the compressibility factor is demonstrated with reference to Figure 3.

The  $P_r$  values listed in Table 1 are entered in separate

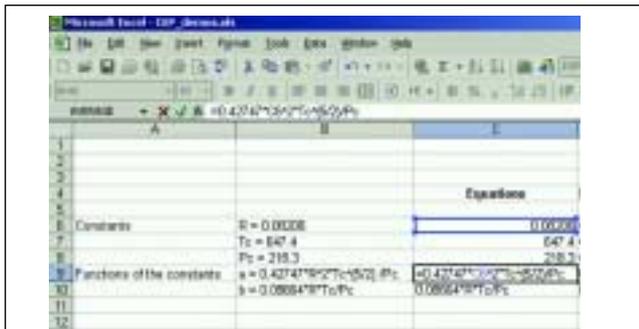


Figure 2. Replacing variable name by cell address by “pointing and clicking.”

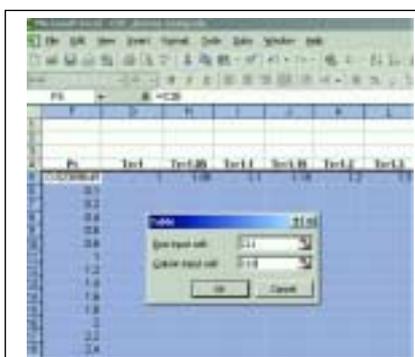


Figure 3. Defining a “Two-Input Data Table” for the calculation of the compressibility factor.

rows in column F and the  $T_r$  values are entered into separate columns in the fifth row. The address of the calculated value of the compressibility factor is entered in the upper corner on the left side of the table (cell F5). Note that the headings entered in the fourth row are not required parts of the table but are used as the “Legend” in the graph to be prepared (Figure 4).

After entering the  $P_r$  and  $T_r$  values and the address of the target result, the whole area of the table is selected and the “Table” option from the “Data” menu is chosen. The

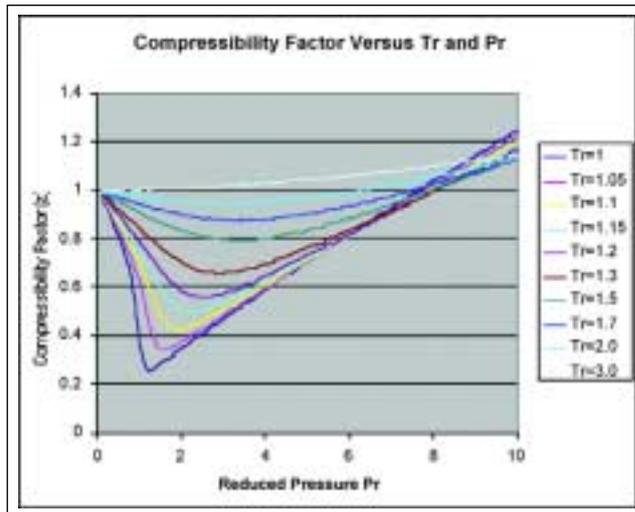


Figure 4. Screenshot of the plot of the compressibility factor vs. the reduced temperature and pressure.

address of the parameter  $T_r$  is specified as the “Row Input Cell,” since the  $T_r$  values are entered in a row, and the address of the parameter  $P_r$  is specified as the “Column Input Cell.” After clicking on the “OK” button, the table is filled with the compressibility factor values corresponding to the respective  $T_r$  and  $P_r$  values.

Plotting the data included in this table yields the graph shown in Figure 4. This type of generalized compressibility factor chart can be found in many handbooks and textbooks of thermodynamics. Tables and charts of enthalpy and entropy departures and fugacity coefficients can be similarly prepared.

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