

Beware of Errors in Numerical Problem-Solving

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Understand how to detect and prevent common errors when using mathematical software tools.

The introduction of mathematical software packages such as Excel, MATLAB and Polymath into the field of engineering problem-solving has brought about many benefits — chief among them the ability to obtain more-precise results more quickly. However, numerical solution techniques have also introduced new sources of errors, which may often go undetected if the user is inexperienced in the use of these new computational tools.

The most common errors in the regression of data originate from the use of regression models with too many or too few parameters (1), fitting polynomial models without proper scaling (standardization) of the data, correlation of data when the model equations are improperly linearized (1), or an experimental design for obtaining data that is not satisfactory (2).

There are many examples in the literature describing the potential challenges involved in solving systems of nonlinear algebraic equations (NLEs). These include identifying good initial guesses and correctly formulating the problem to enable convergence (3). Even if a solution is found, it may not be feasible in the physical sense (e.g., negative concentrations) or it may be a false solution caused by improper variable and/or function scaling.

The most common source of errors in solving ordinary differential equations (ODEs) is the indiscriminate use of default error tolerances of the ODE solver tools (4). Failure to use the proper integration algorithm (stiff vs. non-stiff), carelessly rounding numbers in the model equations, using the model outside the domain of its validity, and the use of inadequate resolution in presenting the results have been documented (1, 5) as additional common sources of errors in solving ODEs

Being aware of potential causes of errors in numerical problem-solving is the first step in detecting and preventing such errors. This article explores three potential causes of errors and proposes means to prevent them.

No consideration given to problem parameter uncertainties

The importance of performing a sensitivity analysis to determine the impacts of small changes in various parameters on the problem's solution has been recognized in the field of optimization. Parameter values usually contain errors and/or uncertainties, making information about the sensitivity of the optimum to changes or variations in a parameter very important to optimal process design (6). However, sensitivity analysis is rarely carried out for other types of problems.

This example demonstrates the importance of a sensitivity analysis in solving systems of nonlinear algebraic equations. The example was originally published by Froment and Bishoff (7), and its solution using Mathcad was presented by Parulekar (8).

Consider the catalytic hydrogenation of an olefin (component A) in an isothermal continuously stirred tank reactor (CSTR). Differential mass balance on component A yields:

$$\frac{dC_A}{dt} = \frac{C_{A0} - C_A}{\tau} - r_A \quad (1)$$

where C_{A0} is the inlet concentration of A (mol/L), $\tau = V/v_0$ is the space time (s), V is the reactor volume (L), v_0 is the inlet flowrate (L/s), and r_A is the reaction rate per unit reactor volume (mol/L-s):

$$r_A = \frac{C_A}{(1 - C_A)^2} \quad (2)$$

The concentration of A at steady state is sought for the operating condition: $C_{A0} = 13$ mol/L, $V = 10$ L, and $v_0 = 0.2$ L/s. Finding the steady-state solution requires solving the nonlinear algebraic equation $f(C_A) = 0$ where:

Computational Methods

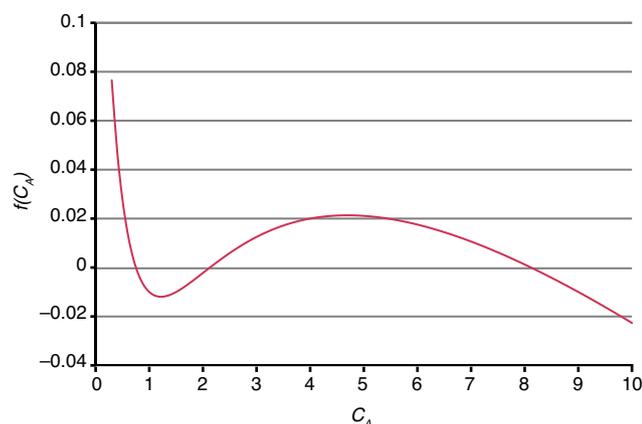
$$f(C_A) = \frac{C_{A0} - C_A}{\tau} - r_A \quad (3)$$

In Figure 1, $f(C_A)$ is plotted vs. C_A for the region $0 \leq C_A \leq 10$, which contains three real solutions. The solutions obtained by the Polymath 6.1 software package are: $C_{A1} = 0.7515358$, $C_{A2} = 2.130933$, and $C_{A3} = 8.117532$. Polymath displays the results showing seven significant digits. Mathcad displays the same results with 20 significant digits. The discrepancy between the number of significant digits in the CSTR parameters (one or two) and the number of digits reported in the solution (up to 20) cannot be overstated.

The number of significant digits reported for the solution should be based, in this case, on the uncertainty associated with the parameter values.

Table 1 presents the values of C_A for various levels of uncertainty in the flowrate, v_0 . If an uncertainty of 10^{-4} L/s is assumed and the corresponding flowrate of 0.2001 L/s is used instead of the base case 0.2 L/s, only the first two digits of the calculated values of C_A match those of the base case. For an uncertainty of 10^{-3} L/s ($v_0 = 0.201$ L/s), the first two roots contain only one matching digit and the largest root two matching digits. For an uncertainty of 10^{-2} L/s, there is not even a single correct digit in the first two roots and only one in the largest root. Thus, considering any realistic estimate of the uncertainty in the flowrate leads to the conclusion that the solutions for C_A should be rounded to two significant digits, as all the additional digits are uncertain.

It is important to understand that this analysis applies only to physical quantities obtained as the final results of the computation. In other cases, rounding may lead to significant errors. This will be demonstrated in a later example.



▲ **Figure 1.** The plot of $f(C_A)$ vs. C_A for $v_0 = 0.2$ L/s reveals that the reaction has three steady states (where the $f(C_A)$ curve crosses the x-axis) in this region: $C_{A1}^* = 0.75$, $C_{A2}^* = 2.13$ and $C_{A3}^* = 8.12$.

The value of the flowrate might be specified by one significant digit because the flowrate was measured (or controlled) with such accuracy. Thus, its value could vary from 0.15 L/s to 0.24 L/s. The last two columns of Table 1 show the calculated C_A for the two extreme values of v_0 . For $v_0 = 0.24$ L/s, there is only one real root at $C_A = 9.36922$ mol/L, while for $v_0 = 0.15$ L/s there is one real root at $C_A = 0.3419$ mol/L. Thus, at this higher level of uncertainty, there is only one root instead of the three roots for the base case of $v_0 = 0.2$ L/s, and the root varies significantly depending on what values of v_0 is used.

Use of inappropriate statistics and graphical representations to analyze regression models

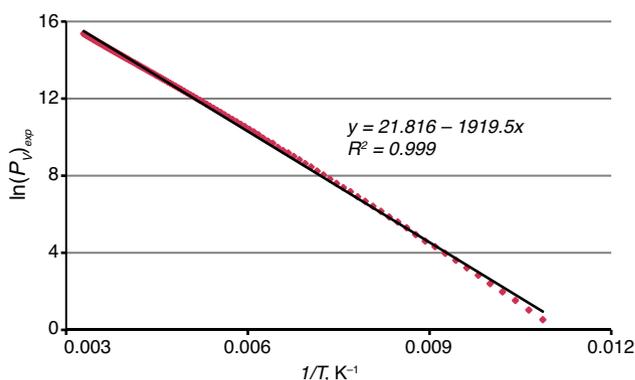
The use of inappropriate statistics and graphical representations often leads to the acceptance of unsatisfactory regression models. This phenomenon is illustrated by fitting the Clausius-Clapeyron equation to vapor pressure (P_V) data for ethane.

Vapor pressure data, containing $N = 107$ points, are available (9) over the temperature range of $T = 92$ K ($P_V = 1.7$ Pa) through $T = 304$ K ($P_V = 4.738 \times 10^6$ Pa). This range essentially covers the liquid-phase region between ethane's triple-point temperature (90.352 K) and its critical temperature (305.32 K). The Clausius-Clapeyron equation is considered inappropriate for modeling vapor pressure over such a wide temperature range, and this can be revealed by certain types of statistics and graphical representations.

The Clausius-Clapeyron equation is given by:

$$\ln(P_V) = A + \frac{B}{T} \quad (4)$$

where A and B are coefficients calculated by regression of experimental data.



▲ **Figure 2.** A plot of $\ln(P_V)_{exp}$ vs. $1/T$ for ethane between the triple point and T_C shows a good representation of the data by a straight line with an R^2 value very close to 1. This seemingly indicates that the Clausius-Clapeyron equation is appropriate to model vapor pressure over the entire range.

Table 1. The appropriate number of digits (shown in bold) depends on the uncertainty in the input parameters.						
Uncertainty	Feed flowrate, v_0 (L/s)					
	0.2	0.2001	0.201	0.21	0.24	0.15
$C_{A, 1st\ Root}$	0.751536	0.7533915	0.7707207	1.162332	—	0.341902
$C_{A, 2nd\ Root}$	2.130933	2.124481	2.066326	1.311824	—	—
$C_{A, 3rd\ Root}$	8.117532	8.122128	8.162953	8.525843	9.369219	—

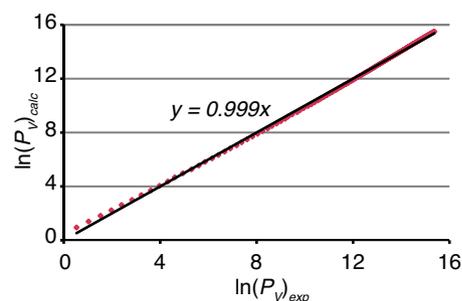


Figure 2 plots $\ln(P_v)_{exp}$ vs. $1/T$ along with the straight line fitted to the data, which is represented by:

$$y_{calc} = 21.816 - 1919.5x \quad (5)$$

where $x = 1/T$ and $y_{calc} = \ln(P_v)_{calc}$. The correlation coefficient, R^2 , is defined as:

$$R^2 = \frac{\sum_{i=1}^N (y_{i,calc} - \mu)^2}{\sum_{i=1}^N (y_i - \mu)^2} \quad (6)$$

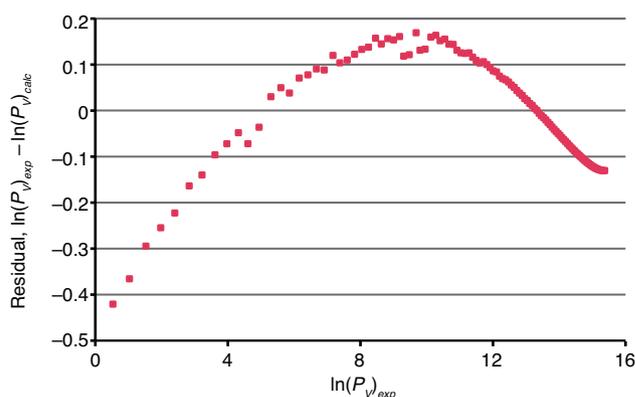
where μ is the sample mean of the dependent variable. The value of R is bounded by $0 \leq R \leq 1$. If R is close to 1, there is strong correlation between the variables, whereas a value close to 0 indicates weak or no correlation. In this case, $R^2 = 0.999$, very close to 1. Thus, the plot of $\ln(P_v)_{exp}$ vs. $1/T$ and the statistical R^2 both indicate that the Clausius-Clapeyron equation represents the vapor pressure data adequately over the entire range from the triple point to T_C .

Another widely used graphical representation for checking the adequacy of a correlation is the plot of the calculated value of the dependent variable, y_{calc} , vs. the experimental value, y . A good fit produces a straight line with a slope close to 1.0.

In Figure 3, $\ln(P_v)_{calc}$ (as calculated by the Clausius-Clapeyron equation) is plotted vs. $\ln(P_v)_{exp}$. The data points are aligned along a straight line with the slope of 0.999 with only small deviations. Thus, this type of representation also indicates a good fit between the Clausius-Clapeyron equation and the vapor pressure data over the entire range. However, comparing $\ln(P_v)_{calc}$ and $\ln(P_v)_{exp}$ at a specific temperature tells a different story. For example, at $T = 92$ K, $\ln(P_v)_{exp} = 0.53$ and $\ln(P_v)_{calc} = 0.95$, which is roughly an 80% difference. This cannot be considered an adequate representation of the experimental data.

A residual plot is the proper graphical means to test the goodness of fit between a regression model and the data. The residual of a sample, ϵ_p , is the difference between the measured sample value and the regressed (fitted) function value:

▲ **Figure 3.** The widely used graphical demonstration of the fit between experimental and calculated data, $\ln(P_v)_{calc}$ calculated by the Clausius-Clapeyron equation vs. $\ln(P_v)_{exp}$, for ethane between the triple point and T_C , indicates that the Clausius-Clapeyron equation can represent the vapor pressure very well over the entire range.



▲ **Figure 4.** The strong curvature of the vapor pressure, which is not explained by the Clausius-Clapeyron equation, is clearly seen in this residual plot for $\ln(P_v)$ calculated by the Clausius-Clapeyron equation for ethane between the triple point and T_C .

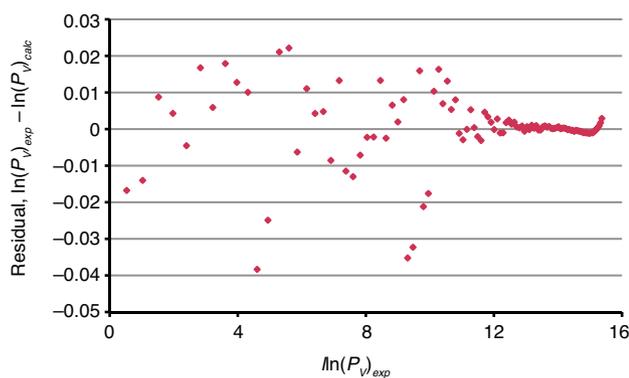
$$\epsilon_i = y_i - y_{i,calc} \quad (7)$$

A random distribution of the residuals around zero indicates that the regression model represents the data correctly. A clear trend or pattern in the residual plot may indicate either the model's lack of fit to the data or that the assumed error distribution for the data (*i.e.*, random error distribution in y) is incorrect. In Figure 4, the residual $\ln(P_v)_{exp} - \ln(P_v)_{calc}$ is plotted vs. $\ln(P_v)_{exp}$. The obvious trend (curvature) in the residuals indicates that the Clausius-Clapeyron equation cannot represent the data adequately.

Careless rounding of model parameters

The Design Institute for Physical Properties Research (DIPPR) database (10) recommends the Riedel equation for modeling vapor pressure data. The Riedel equation can be written as:

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▲ **Figure 5.** A residual plot for $\ln(P_V)$ calculated by the Riedel equation for ethane between the triple point and T_C shows that the residuals are randomly distributed, and they are smaller by at least an order of magnitude. This demonstrates that the Riedel equation is a much better representation than the Clausius-Clapeyron equation.

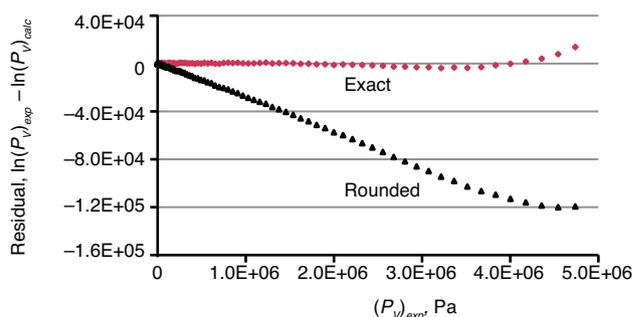
$$\ln(P_V) = A + \frac{B}{T} + C \ln T + DT^E \quad (8)$$

where A , B , C , D and E are the parameters of the regression model. Usually the value of E is set at 2 to allow the rest of the parameters to be calculated by linear regression. Using the same vapor pressure data (9), the following parameter values were calculated: $A = 5.1857\text{E}+01$, $B = -2.5987\text{E}+03$, $C = -5.1283\text{E}+00$, and $D = 1.4913\text{E}-05$.

Figure 5 plots the residual of $\ln(P_V)$ calculated by the Riedel equation using the DIPPR parameter values. These residuals are at least an order of magnitude less than the residuals obtained when $\ln(P_V)$ was calculated by the Clausius-Clapeyron equation. This plot has two distinct regions. In the first region (up to $\ln(P_V) \approx 12$), the residuals are in the range of -0.04 to 0.02 and do not show any particular pattern or trend. In the second region ($\ln(P_V) > 12$), the residual values are an order of magnitude lower — all have an absolute value less than 0.003 — and show a clear pattern. To obtain a completely random distribution of the residuals, a different correlation should be used; however, improving the correlation by using a different type of equation is outside of the scope of this article.

Although the copy-and-paste function is a very convenient and time-saving option when transferring data between databases and software packages, it can introduce rounding errors. For example, the Riedel equation constants for various compounds can be copied from the DIPPR database and pasted into an Excel spreadsheet, which stores the values exactly as they appear in the DIPPR database. However, when the default number-display format is used, they are displayed rounded to two or three decimal places: $A = 5.19\text{E}+01$, $B = -2.60\text{E}+03$, $C = -5.13\text{E}+00$, and $D = 1.49\text{E}-05$. When these values are subsequently copied from Excel and pasted into a document or a different software package, the additional digits are lost.

Using rounded values of the parameters leads to signifi-



▲ **Figure 6.** In a residual plot for P_V calculated by the Riedel equation for ethane between the triple point and the T_C , rounding the Riedel equation parameters causes the residual (the error) to increase by orders of magnitude.

cant errors in the calculated vapor pressure values. Figure 6 compares the residuals plots of P_V calculated using exact and rounded parameter values. At the higher pressures, the residual (error) when rounded parameter values are used is on the order of 2.5%, compared with 0.3% when exact parameter values are used. Thus, in this example, careless rounding causes the prediction error to increase by almost an order of magnitude.

Exporting property data to computer code quickly and accurately

It is important to simplify data transfer from a database to computer code to minimize the probability of introducing errors during this process, including unintended rounding of model parameters.

We have developed an interface called “DIPPR to Code” that enables searching the DIPPR database for a particular compound, marking the desired properties, and obtaining as output the necessary data and correlations in a format that can be copied and pasted directly into computer code. Polymath and MATLAB codes are currently supported, and Excel code is available through export from Polymath. Property correlation equations coded in MATLAB format can also be introduced into programs written in various computer languages with very minimal changes. Thus, the DIPPR to Code interface enables exporting DIPPR data and equations to many widely used software packages.

To illustrate, let's say we are using Polymath and we need the vapor pressure of ethane as a function of temperature. DIPPR to Code allows the user to query the DIPPR database for a particular chemical species and the desired property; the desired temperature can be specified or the temperature dependency of this property can be requested. The information that is provided by the interface program in the Polymath format for the vapor pressure of ethane is shown in Table 2. The code generated by the interface includes correlation equations, definitions of constant values, and comments. (Each comment starts with a # sign and ends with the end of the line. The row numbers are not part of the output generated by the interface program, but are shown

Table 2. The vapor pressure of ethane can be obtained from the DIPPR database by the "DIPPR to Code" interface in a format suitable for use in Polymath.

Output Line No.	Equation / # Comment
1	# Liquid Vapor Pressure of C2H6
2	# ETHANE
3	# Error: < 1%; Data Type: Smoothed; Source Type: Evaluated; Source Detail: Evaluated; Error Source: Staff
4	# Min_T = 90.35, Max_T = 305.32, Min_Val = 1.1273, Max_Val = 4852200 [K ; Pa]
5	VP_C2H6 = exp(51.857 - 2598.7 / T - 5.1283 * ln(T) + 1.4913E-05 * T ^ 2) # Pa

here as references for the following explanation.)

Line 1 is the full name of the property and the formula of the compound (as a comment), and Line 2 is the full name of the compound. Line 3 contains information on the reliability of the vapor pressure correlation that was obtained from the DIPPR database. Line 4 shows the range of validity of the correlation equation — the lower temperature limit of the range of validity (*Min_T*), the upper temperature limit (*Max_T*), the property (vapor pressure, in this case) value at the lower temperature limit (*Min_Val*), and the property value at the upper temperature limit (*Max_Val*) — as well as the units of the variables (K for temperature and Pa for pressure).

The resulting property correlation equation for ethane vapor pressure is shown in Line 5. The calculated value of the vapor pressure is entered into a variable comprised of the sym-

bol of the property (*VP* in this case) and the chemical formula of the compound. The equation is presented in a form that is readily transferable into Polymath code. The coefficients of the equation are shown in the same number of digits as they are stored in the database, so no rounding error is introduced.

Final thoughts

A complete problem definition should specify the uncertainty in the value of each of the parameters, which will enable a determination of the uncertainty in the solution. This, in turn, indicates the number of significant digits to be used in reporting the results. Ultimately, it may be revealed that a proposed process should not be implemented because of levels of uncertainty that are too high.

The correlation coefficient (R^2) and a simple plot of calculated values vs. experimental values can be misleading in determining the goodness of the fit between the data and the regression model. The residual plot is the most reliable means for examining the goodness of the fit.

Beware of rounding errors, especially the unintended rounding that often occurs when copying and pasting data between databases, documents and programs.

Proper attention to the potential causes of errors presented here and in previous articles (1–5) can considerably improve the reliability of the results in numerical problem-solving and in the correlation of data by regression.

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