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Several Applications of Advanced Scientific Calculators: Nonlinear Least-Squares Analysis and Titration of a Weak Acid

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Abstract: Several advanced applications of scientific graphing calculators are demonstrated. These include (a) nonlinear least squares analysis and (b) construction of titration curves for weak acids with a strong base. Stepwise instructions for obtaining the titration curves with TI-80 Series Calculators are presented. Immediate display of graphical results of a solution from a quantitative chemical problem in a classroom setting is one of the advantages of the advanced scientific calculator.

Introduction

Recently we presented a comprehensive comparison of various types of scientific calculators [1]. It was demonstrated that the advanced graphing calculator (ASC) can handle several problems in chemistry much more efficiently than lower-level calculators such as basic scientific calculators (BSCs) or intermediate scientific calculators (ISCs) [1]. Interested readers should refer to reference 1 for an explanation of the differences between the three types of calculators and their limitations. The applications discussed in this article were (a) an equilibrium problem using the numerical method, (b) simulation of titration curves for a strong acid with a strong base, and (c) a graphic display of the time course of a concentration profile of the reactants and products for a first-order reaction. Previously, other authors have presented several other applications [2, 3]. These include a graphing method for solubility and acid–base equilibrium problems [2] and a study of first-order kinetics with CBL technology [3]. In this paper, we extend our previous work [1] to consider other advanced applications of the advanced graphing calculator (ASC). These include nonlinear least-squares analysis and the simulation of titration curves for a weak acid with a strong base.

Regression Analysis Using a Nonlinear Least-Squares Method

Finding the best-fit smooth line through a set of scattered data points is common practice among experimental scientists, engineers and students, and the linear least-squares method [4] has been available on scientific calculators since their advent in the seventies [1]. Many papers on this subject have appeared in the *Journal of Chemical Education* [5–11]. Some of the articles [10, 11] and monographs [12, 13] are based on the usage of spreadsheet programs such as QuattroPro or Microsoft Excel. None of the papers, however, dealt with the use of ASCs for a nonlinear regression analysis.

One of the most important features of ASCs is the availability of a nonlinear regression package as well as a simple linear one. Depending on the model, TI-80 series calculators [14] are capable of handling up to five to twelve different nonlinear mathematical functions, which is commonly encountered in science and engineering. Even though the program has a limitation in that it cannot handle a user-defined function, the package is very useful, in particular because of the presence of the exponential function. The exponential function is one of the most commonly used in science and engineering. For more nonlinear functional relations encountered in chemistry one may refer to reference 6. In chemistry, the exponential function is typically associated with the treatment of first-order kinetics, Arrhenius-type equations for the determination of activation energies from rate constants or of standard free energies from equilibrium constants.

Example. (This example is adapted from reference 15 with some modifications in the data in order to give more scattering in the data by adding noise.)

Decomposition of hydrogen peroxide is a first-order reaction. From the concentration, [A], versus time, *t*, data given in the first two columns, find the first order-rate constant, *k*, and the half life, $t_{1/2}$.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (1)$$

t (min)	$[A]_t$ (M)	$\ln [A]_t$
0	1.00	0.000
2	0.91	–0.095
5	0.72	–0.329
10	0.64	–0.446
20	0.31	–1.171
30	0.25	–1.386
40	0.10	–2.303
50	0.082	–2.501
60	0.050	–2.999

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With a basic scientific calculator in which only linear regression is available, the concentration must be converted to its logarithm (i.e., the third column above), then the linear form of the first-order rate equation given in terms of the logarithm can be used:

$$\ln [A]_t = -kt + \ln [A]_o \qquad (2)$$

The results of a least-squares analysis using this linear function yield a value of –0.025 for the intercept, –0.051 min^{-1} for the slope, and –0.994 for the correlation coefficient. It may be noted that, unlike in a regression analysis with a PC spreadsheet program (i.e., Quattro Pro or Excel), the output with the calculator yields only the values of the parameters without the uncertainties associated with the parameters. The rate constant from the slope of the plot of ln $[A]_t$ versus t is

$$k = -(\text{slope}) = 0.051\ \text{min}^{-1} \qquad (3)$$

which yields with a half life, $t_{1/2}$, of 13.6 min.

With an ASC, however, it is not necessary to convert concentration to ln (concentration) because of the availability of the exponential function for regression. One can fit the original exponential form of the first-order equation directly to the raw $[A]_t$ versus t data without any further treatment of the original data. Bypassing the step of taking the logarithm of the concentrations saves a substantial amount of time.

$$[A]_t = [A]_o e^{-kt} = [A]_o (e^{-k})^t \qquad (4)$$

which corresponds to the general form

$$y = ab^x \quad \text{or} \quad [A]_t = ab^t \qquad (5)$$

where the two parameters, a and b, are

$$a = [A]_o \qquad (6)$$

and

$$b = e^{-k} \qquad (7)$$

Then,

$$k = -\ln b \qquad (8)$$

The basic stepwise instructions for performing this operation on a TI-85 calculator follow. Although the input mode for other models (Models 81, 82, 83, 83 Plus, 86, and 89) may differ somewhat from the TI-85, the frame work is basically same.

Step 1. Press the STAT key.

Step 2. Select EDIT, press ENTER.

Step 3. Enter all of the values of the independent (x) and dependent (y) variables.

Step 4. Press the STAT key again. This step is not necessary for the TI-85 or higher.

Step 5. Select CALC.

Step 6. Execute by selecting EXPREG or EXPR depending the model number

for a regression with the exponential function.

Output for the regression yields

a = 0.975 (M), b = 0.9506, r = –0.9938 (the correlation coefficient).

Therefore,

$$k = -\ln (0.9506) = 5.07 \times 10^{-2}\ (\text{min}^{-1}) = 8.44 \times 10^{-4}\ (\text{sec}^{-1}) \qquad (9)$$

$$t_{1/2} = 0.693/k = 0.693/(8.44 \times 10^{-4}\ \text{s}^{-1}) = 821\ \text{s} = 13.68\ \text{min} \qquad (10)$$

The results are the same as those from linear regression analysis with eq 2, which is much more time-consuming. The graphic output for the comparison of the theoretical and experimental concentrations is given in Figure 1.

Titration Curves for Weak Diprotic and Polyprotic Acids

Because titration curves for a strong acid with a strong base have already been presented (refer to the animation in reference1, we now report titration of weak acids with strong bases.

Example. V_a mL of a M_a molar triprotic acid, H_3A, solution is being titrated with a M_b molar standard solution of a strong base. Construct a titration curve. Specifically, construct a titration curve for a solution of 25.00 mL of 0.100M H_3PO_4 titrated with a 0.100 M standard solution of NaOH.

An exact solution for the hydrogen ion concentration for an equilibrium involving a titration of a weak acid, mono- or polyprotic, generally yields higher order (cubic or above) equations [16–18] that can be solved numerically. Numerical methods are often employed using a PC for this type of problem, and we have reported one such example using the bisection algorithm [19]. On the other hand, a different approach (an inverse method), has often been adopted by others in order to avoid numerical solutions for higher-order equations. In the inverse method, the hydrogen ion concentration ($[H^+]$), instead of the base volume, is taken as an independent variable, and the base volume is taken as a dependent variable [16, 18, 20, 21]; hence, the volume of the base is calculated as a function of the hydrogen ion concentration. This inverse approach is better suited to ASCs than the more time-consuming numerical approach because an ASC is very limited in speed and RAM compared to a PC or mainframe computer. Thus, we adopted this inverse approach.

The following general relationship between all the variables involved in the titration of a weak acid can be found in several articles and books on analytical chemistry [18, 20, 21]. Interested readers should refer to the original references for the derivation.

$$V_b(C_b + [H^+] - K_w/[H^+]) = V_a(C_aF - [H^+] + K_w/[H^+]) \qquad (11)$$

where

$$F = K_1/([H^+] + K_1) \text{ for a monoprotic acid} \qquad (12)$$

or

$$F = (K_1[H^+]^2 + 2K_1K_2[H^+] + 3K_1K_2K_3)/([H^+]^3 + K_1[H^+]^2 + K_1K_2\,[H^+] + K_1K_2K_3) \text{ for a triprotic acid} \qquad (13)$$

All constants (K_w , K_1, K_2, and K_3) have their usual meaning. Solving eq 11 for V_b,

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$$V_b = V_a(C_aF - [H^+] + K_w/[H^+]) / (C_b + [H^+] - K_w/[H^+]) \qquad (14)$$

V_b is calculated at various $[H^+]$ (hence pH) using eq 14.

This can be implemented on an ASC with the following set of instructions. The italicized part of the instructions should be written on the display screen in the normal on-screen editing mode. These instructions are written for all TI-80 series calculators. The basic framework should be applicable to any ASC regardless of manufacturer. Because the input formats are slightly different among the TI series models, we provide two set of instructions, one for TI-85 or higher series and the other one for the TI-83 or lower series. TI-83 and TI-83 Plus have recently been the most popular on high school and college campuses. The reader should be reasonably familiar with basic use of the calculators in order to be able to follow the instructions.

Instructions for TI-85 or Higher Series

Information displayed on the screen is indicated with italics.

Step 1: Execute the Clear Draw command to erase any picture left on the graphic screen by typing (or by simply calling) *ClDrw* and pressing ENTER. If other functions (y_i) in the GRAPH are on, please turn them off.

Step 2: Adjust the range and scale for the view on the screen after selecting the RANGE:
Xmin=0, *Xmax=100*, *Xscl =5* for the *x* axis (V_b, mL)
Ymin = 0, Ymax = 14, Yscl = 1 for the *y* axis (pH).

Step 3: Load the parameters and constants into the memory using the STO(→) or = keys.

$$25 \rightarrow VA;\ 0. \rightarrow CA;\ 0.1 \rightarrow CB \qquad (15)$$

$$10^{-14} \rightarrow KW;\ 6.9\text{x}10^{-3} \rightarrow K1;\ 6.2\text{x}10^{-8} \rightarrow K2;\ 4.8\text{x}10^{-13} \rightarrow K3 \qquad (16)$$

$VA=25$; $KW = 10^{-14}$ etc. will work as well if using the = key)

Step 4: Load the parameters *H* and *F* (eq 13) as a function of *x* and *H*, respectively

$$H=10^{-x} \text{ (this will be displayed as H = 10^x)} \qquad (17)$$

where *x* is the pH and $H = [H^+]$.

$$F = (K1*H^2+2K1*K2*H+3K1*K2*K3)/$$
$$(H{}^\wedge3+K1*H^2+K1*K2*H+K1*K2*K3) \qquad (18)$$

Step 5: Load the dependent variable (V_b) using the following:

$$VB=VA(CA*F-H+KW/H)/(CB+H-KW/H) \qquad (19)$$

Step 6: For a normal conventional display (i.e., pH versus volume), invoke the Draw Inverse Function (DrInv) command.
DrInv VB, Then press ENTER

Step 7: To generate an unconventional display with pH being the *x* axis and volume being the *y* axis,use the following:
Call the Draw Function (DrawF) command on the screen.
DrawF VB, Then press ENTER.

The range must be readjusted for the proper display view within the screen.
Xmin=0, *Xmax=14*, *Xscl=1* for the *x* axis (pH)
Ymin=0, Ymax=100, Yscl=5 for the *y* axis (V_b, mL).

Instructions for the TI-83 and TI-83 Plus or Lower Series

Step 1: Execute the Clear Draw command to erase any picture left on the graphic screen by typing (or by simply calling) *ClrDraw* and pressing ENTER. If other functions (Y_i) are active for a display, please turn them off.

Step 2: Adjust the range and scale for the screen view after pressing WINDOW:
Xmin=0, *Xmax=100*, *Xscl=5* for the *x* axis (V_b, mL)
Ymin=0, Ymax=14, Yscl=1 for the *y* axis (pH).

Step 3: Load the parameters and constants into the memory using the STO(→) or = keys.

$$25 \rightarrow V;\ 0.1 \rightarrow M;\ 0.1 \rightarrow N \qquad (15')$$

$$10^{-14} \rightarrow K;\ 6.9\text{x}10^{-3} \rightarrow Q;\ 6.2\text{x}10^{-8} \rightarrow R;\ 4.8\text{x}10^{-13} \rightarrow S \qquad (16')$$

(Note: Unlike with the TI-85, names user-defined variables must be a single letter on the TI-83. Input using the equals sign (=) is not available on the TI-83.)

Step 4: Load the variables Y_1 (= $[H^+]$) and Y_2 (= *F*, eq 13), as a function of *x* and Y_1 respectively.

$$Y=10^{-x} \text{ (this will be displayed as } Y_1 = 10\text{^}(-x)\text{)} \qquad (17')$$

where *x* is the pH

$$Y_2=(Q*Y_1^2+2Q*R*Y_1+3Q*R*S)/$$
$$(Y_1{}^\wedge3+Q*Y_1^2+Q*R*Y_1+Q*R*S) \qquad (18')$$

Step 5: Load the dependent variable, Y_3(= V_b) using the following:

$$Y_3=V*(M*Y_2-Y_1+K/Y_1)/(N+Y_1-K/Y_1) \qquad (19')$$

Step 6: For a normal conventional display of pH versus volume, invoke the Draw Inverse Function (DrawInv) command, *DrawInv* Y_3, Then press ENTER.

The Draw Inverse Function is available only with TI-83 or higher series.

Step 7: For TI-82 or lower series, only the unconventional display (with pH being the *x* axis and volume being the *y* axis) is available.

Call the Draw Function (DrawF) command on the screen.
DrawF Y_3 Then press ENTER.

The range must be readjusted for the proper display view within the screen:
Xmin=0, Xmax=14, Xscl=1 for *x* axis (pH)
Ymin=0, Ymax=100, Yscl=5 for *y* axis (V_b, mL).

The progress of a titration can be gradually displayed point by point as the calculation proceeds. It is better to be in the LINE display mode, as opposed to the POINT display mode, in order to view the gradual progress of the entire titration. By setting K2 = K3 = 0, one can generate titration curves of a weak monoprotic acid at various K_a (or pK_a) values. Typical titration curves from this method are shown in Figure 2, in which the volume of the acid used is 50.0 mL instead of 25.0 mL. In Figure 3, titration curves for various acids are presented starting with acetic acid (pK_a = 4.75, Curve a). Curve b is for phosphoric acid with three pK_a values: 2.16, 7.20, and 12.3. It should be noted that the third equivalence point for phosphoric acid is not observable because the separation between its pK_3 (12.3) and pK_w [14] is not wide enough. Curve c is for an imaginary acid with well-separated pK_a values in order to show three distinct equivalence points. The difference between two

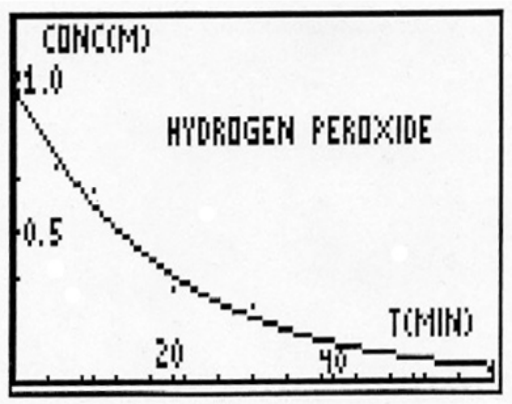

Figure 1. Direct fit of the exponential form of a first-order rate equation to concentration versus time data for the decomposition of hydrogen peroxide. The dots represent the raw data. The line is the best fit line with a = 0.975 M and $k = b = 8.44 \times 10^{-4}$sec^{-1}. The correlation coefficient for the fit is c =-0.994.

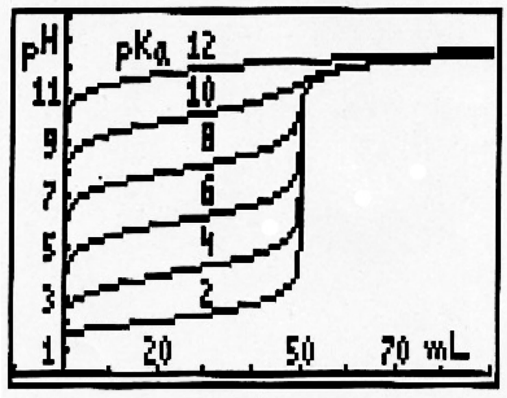

Figure 2. Titration of 50 mL of solutions of several weak monoprotic acids (0.100 M each) with various dissociation constants, Ka, with a standard solution of a strong base (0.100 M NaOH). From the bottom, $K_a = 10^{-2}$, pK_a = 2; $K_a = 10^{-4}$, pK_a = 4; $K_a = 10^{-6}$, pK_a=6; $K_a = 10^{-8}$, pK_a = 8; $K_a = 10^{-10}$, pK_a=10; $K_a = 10^{-12}$, pK_a = 12.

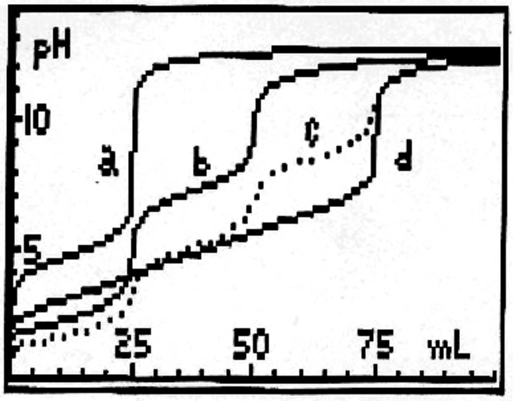

Figure 3. Titration of 25.0 mL of a solution of several weak acids (0.100M each) with a standard solution of a strong base (0.100 M NaOH). (a) 0.100 M CH_3COOH, $K_1 = 1.8 \times 10^{-5}$ (pK_1 = 4.75), $K_2 = K_3$ = 0; (b) 0.100 M H_3PO_4, $K_1 = 6.9 \times 10^{-3}$ (pK_1 = 2.16), $K_2 = 6.2 \times 10^{-8}$ (pK_2 = 7.20), $K_3 = 4.8 \times 10^{-13}$ (pK_3 = 12.3); (c) an 0.100 M acid with $K_1 = 1.0 \times 10^{-1}$ (pK_1 = 1.00), $K_2 = 3.2 \times 10^{-5}$ (pK_2 = 4.50), $K_3 = 1.0 \times 10^{-8}$ (pK_3 = 8.00); (d) 0.100 M $C_3H_4(OH)(COOH)_3$ (citric acid), $K_1 = 7.4 \times 10^{-4}$ (pK_1=3.13), $K_2 = 1.7 \times 10^{-5}$ (pK_2=4.10), $K_3 = 3.5 \times 10^{-7}$ (pK_3 = 6.46).

adjacent pK_a values should be larger than 3 for the equivalence point to be visible. For citric acid (Curve d) the first two equivalence points are not detectable because the three pK_a values (3.13, 4.10, and 6.46, respectively) are so close; only the third equivalence point can be detected thanks to the wide gap between pK_3 (6.46) and pK_w (14.0).

To print the graphs, a TI calculator can be interfaced to a PC/printer with the TI-GRAPH LINK hardware/software [22]. All three figures are directly from display on the screen with out any editing of the image files with PC software.

Conclusions

The nonlinear least-squares analysis program of the advanced scientific calculator can handle several chemical problems much more efficiently than the linear least-squares analysis program. The inverse method of building a titration curve for a weak acid with a strong base is an example of such a problem. Overhead projection of the calculator's screen is very effective for showing the progressive results of a titration in the classroom setting. Utilizing the display, several aspects of the shapes of the titration curves can be illustrated.

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