

Fitting and Analyzing pH Titration Curves on a Graphing Calculator

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Abstract: The pH titration curve is a well-known figure in chemistry. It is easy to plot this graph from experimental data by measuring pH as a function volume of added titrant; however, there is no simple mathematical equation for expressing pH as a function of titrant volume. The logistic function has been suggested but, as discussed in this paper, it is inadequate for modeling titration curves. Developed in this paper is a piecewise continuous function (with chemically meaningful parameters) of pH versus volume. A program has been written to display this function on a graphing calculator. This program can be used by students (1) to analyze the characteristics of pH titration curves, for example, the derivative and the presence of two inflection points, and (2) to interactively fit experimental titration data that they have collected.

One of the more interesting graphs that occur in chemistry is the pH titration curve shown in Figure 1. This graph shows how pH changes with volume during a titration. In a titration, a chemist is reacting an acid (or base) of unknown concentration with a base (or an acid) of known concentration. At the equivalence point, the number of H^+ ions from the acid is “equivalent” to the number of OH^- ions from the base. This equivalence allows the chemist to determine the concentration of the unknown acid or base. The equivalence point can be recognized easily on the graph as the region where the pH changes most rapidly. Mathematically, the equivalence point is an inflection point on the curve.

Using the Texas Instruments (TI) Calculator-Based Laboratory (CBL) System with a pH probe and TI graphing calculator, it is quite easy to collect pH versus volume data experimentally during a titration. It would be convenient to have a general equation that could be used to model this data. One advantage of a function describing the pH curve is that the experimenter could use the many mathematical features, such as the derivative and trace, of graphing calculators to analyze the titration curve. The logistic function, which produces an S-shaped curve much like a titration curve, can be determined through regression analysis on a graphing calculator. This function has been used to fit titration data, but as discussed in this paper, it is not a very good model for an acid–base titration.

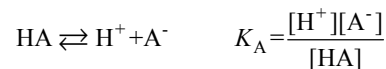
The mathematical analysis of titration curves has been described in many articles and books. One of the most comprehensive of these is the article by Robert de Levie [1] that gives general expressions for many types of titration curves. A recent article by de Levie [2] describes a general simulator for acid–base titrations and P. Glaister [3] has published a unified titration formula for acid–base titrations. These unified equations are based on calculating progress curves, V_B (volume of added base) as a function of H^+ concentration (or pH), as distinguished from titration curves, pH as a function of V_B . Glaister [4] has shown how the progress-curve equation can be inverted to determine the H^+ concentration as a function of V_B . One difficulty of Glaister’s approach is that it requires the solution of a cubic equation.

Kent Crippen, Robert Mann, and David Brooks [5] describe the use of graphing calculators to model titration curves using a calculator program, titrate.83g, that they have written for the TI-83 calculator. This program solves for V_B as a function of pH (the progress-curve approach) and stores the ordered pairs in lists on the calculator. The titration curve is then produced by doing a connect-the-points plot with pH on the y axis and V_B on the x axis.

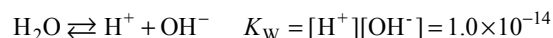
This paper presents a new calculator titration program that produces a general titration function (pH as a function of V_B) that does model correctly the titration of strong and weak acids by a strong base and does not require finding roots of cubic polynomials (except at the equivalence point). This function can be easily programmed on a graphing calculator and used to analyze the properties of pH curves and to determine the unknown concentration of an acid using the tools built in on the TI-83 and TI-86 calculators. The programs (titrafcn.86p for the TI-86 and titrafcn.83p for the TI-83) are available for download [6]. As a final point, we will discuss the characteristics of the logistic function and show in what ways this function is inadequate for modeling titration curves.

pH Titration Curves

In this paper we will consider two types of titrations: (1) a strong acid titrated with a strong base and (2) a weak acid titrated with a strong base. We will assume the strong base is NaOH and that the acids are monoprotic. Let C_A be the concentration of the acid, C_B be the concentration of the base, V_A be the initial volume of the acid, K_A be the acid ionization constant



and K_W be the water ionization constant.



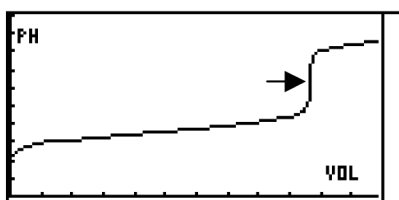


Figure 1. Graph of a titration curve for a weak acid with a strong base on a TI-86 graphing calculator. The arrow points to the equivalence point.

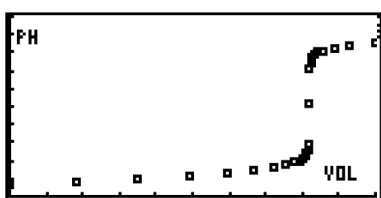


Figure 2. pH versus V_B for a strong acid titrated with a strong base.

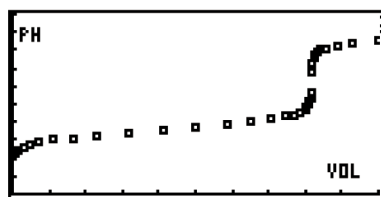


Figure 3. pH versus V_B for a weak acid titrated with a strong base.

In this paper we have simplified the equations for equilibrium constants by using concentrations instead of activities. During a titration, one gradually adds the base to the acid solution and measures the changes in pH of the solution. The volume of base added, V_B , is the independent variable and pH is the dependent variable. The symbol pH is the negative base-10 logarithm of the H^+ concentration, that is

$$pH = -\log_{10} [H^+]$$

The results for the titration of a strong acid and the weak acid ($K_A = 1 \times 10^{-5}$) with $C_A = 0.100$ M, $V_A = 100$ mL, and $C_B = 0.100$ M are shown in Figures 2 and 3.

A pH Titration Function

We will begin the derivation of a pH titration function with the charge balance equation.

$$[Na^+] + [H^+] = [A^-] + [OH^-] \quad (1)$$

Next we will rewrite the concentrations of Na^+ , A^- , and OH^- in terms of C_A , C_B , V_A , K_A , and K_W using the material balance and the ionization equilibrium relationships. The Na^+ concentration is determined from the relationship that the moles of Na^+ are always equal to the moles of added base ($C_B V_B$).

$$[Na^+] = C_B V_B / (V_A + V_B) \quad (2)$$

During the titration, the moles of HA and A^- will be equal to the initial moles of acid ($C_A V_A$).

$$C_A V_A = ([HA] + [A^-])(V_A + V_B) \quad (3)$$

The concentration of HA can be replaced by $[H^+][A^-]/K_A$.

$$C_A V_A = ([H^+][A^-]/K_A + [A^-])(V_A + V_B) \quad (4)$$

Solving eq 4 for the A^- concentration yields the following equation.

$$[A^-] = [C_A V_A / (V_A + V_B)] [K_A / (K_A + [H^+])] \quad (5)$$

And finally we can use the K_W relationship to solve for $[OH^-]$.

$$[OH^-] = K_W / [H^+] \quad (6)$$

Inserting the results of eqs 2, 5, and 6 into eq 1 yields eq 7.

$$C_B V_B / (V_A + V_B) + [H^+] = [C_A V_A / (V_A + V_B)] [K_A / (K_A + [H^+])] + K_W / [H^+] \quad (7)$$

Multiplying both sides of this equation by $(V_A + V_B)(K_A + [H^+])[H^+]$ gives a cubic equation in $[H^+]$.

$$[H^+]^3 + [H^+]^2 [K_A + C_B V_B / (V_A + V_B)] + [H^+] \{ K_A [(C_B V_B - C_A V_A) / (V_A + V_B)] - K_W \} - K_A K_W = 0 \quad (8)$$

Solving this cubic equation for $[H^+]$ gives the H^+ concentration (and therefore the pH) as a function of the volume of added base, V_B . The equivalence point occurs when $C_B V_B = C_A V_A$. The pH at the equivalence point can be determined by solving a reduced form of eq 8.

$$[H^+]^3 + [H^+]^2 [K_A + C_A C_B / (C_A + C_B)] - [H^+] K_W - K_A K_W = 0 \quad (9)$$

The TI-83 and 86 calculators have the capability of solving these cubic equations numerically. Unfortunately, this process is somewhat time consuming. Fortunately though, eq 8 can be approximated. The first step is to divide eq 8 through by $[H^+]$.

$$[H^+]^2 + [H^+] [K_A + C_B V_B / (V_A + V_B)] + K_A [(C_B V_B - C_A V_A) / (V_A + V_B)] - K_W (1 + K_A / [H^+]) = 0 \quad (10)$$

In the initial (acid) region of the titration, where $[H^+] > 10^{-7}$, the last term $K_W (1 + K_A / [H^+])$ will be small and can be neglected. With this approximation we get a quadratic equation that can be solved analytically.

$$[H^+] = 0.5 * [-Y_3 + \sqrt{Y_3^2 + 4K_A Y_1 / Y_2}] \quad (11)$$

$$Y_1 = (C_A V_A - C_B V_B) \quad Y_2 = (V_A + V_B)$$

$$Y_3 = K_A + C_B V_B / (V_A + V_B)$$

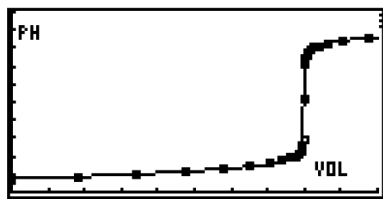


Figure 4. Fit of pH function (solid line) to the titration data points (boxes) for a strong acid titration.

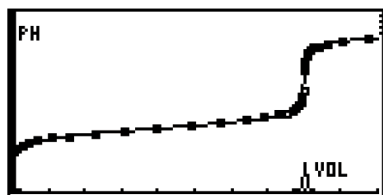


Figure 6. Plot of pH function and first derivative for a weak acid titration.

Table 1. pH of an Acetic Acid Solution after 10.0 mL Increments of 0.100 M Sodium Hydroxide are added

V_B/mL	pH
0.00	2.82
10.0	4.02
20.0	4.41
30.0	4.69
40.0	4.96
50.0	5.28
60.0	5.84
70.0	11.62
80.0	12.06

The approximation cannot be used at the equivalence point or in the region beyond the equivalence point where $[\text{H}^+] < 10^{-7}$; however, in this basic region of the titration, there is another approximation that can be used. If we follow the same steps as given before to derive eq 8 from eq 1 but this time solve for the $[\text{OH}^-]$ instead of $[\text{H}^+]$, we get the following equation for the OH^- concentration.

$$[\text{OH}^-]^2 + [\text{OH}^-][K_B - (C_B V_B - C_A V_A)/(V_A + V_B)] - K_B C_B V_B / (V_A + V_B) - K_W(1 + K_B/[\text{OH}^-]) = 0 \quad (12)$$

Notice the similarity to eq 10. Note that $K_B = K_W/K_A$. For neutral and basic pH values, the last term is small and we can again write an analytical solution to the quadratic equation. This time we are solving for the $[\text{OH}^-]$ to determine the pH of the solution.

$$[\text{OH}^-] = 0.5 \left[-Y_5 + \sqrt{Y_5^2 + 4K_B C_B V_B / (V_A + V_B)} \right] \quad (13)$$

$$Y_5 = K_B - (C_B V_B - C_A V_A)/(V_A + V_B)$$

The complete pH function is determined by three equations, eqs 9, 11, and 13, which are combined to form a single, piecewise equation on the TI graphing calculators ($\Upsilon 7$ in the program titrfacn.83p on a TI-83 and $\Upsilon 7$ in titrfacn.86p on a TI-86). Notice in Figures 4 and 5 the excellent fit of this equation

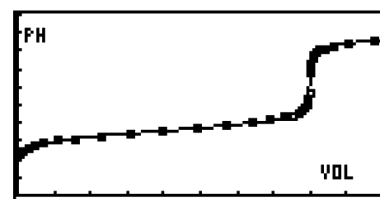


Figure 5. Fit of pH function (solid line) to the titration data points (boxes) for a weak acid titration.

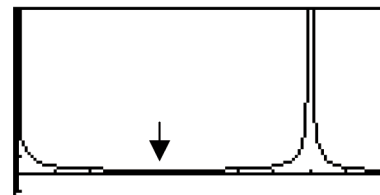


Figure 7. First derivative of the pH titration function. The arrow marks the halfway point (the buffer region).

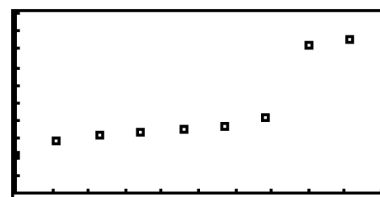


Figure 8. Plot of pH versus volume of base added for an unknown weak acid.

(the line) to the data points (the boxes) for both the strong acid and weak acid titrations.

Figure 6 shows a plot of the first derivative (using $nDer(y7, x, x)$ on the TI-86). As we would expect, the maximum of the first derivative (the small peak near the VOL label) occurs at the equivalence point. If we change the window, more details of the first derivative of the pH curve can be seen as shown in Figure 7. Notice the point halfway to the equivalence point. At the halfway point the concentrations of the acid, HA, and its conjugate base, A^- , are equal. The derivative reaches a minimum at this point. This region, where there is the smallest change of pH with volume of base added, is known as the *buffer region* of the titration curve. Buffers are solutions that resist changes in pH, that is, they have small changes of pH with volume of base (or acid) added. Buffers in our blood maintain the pH level of the blood between 7.35 and 7.45. Note that the halfway point is also an inflection point on the pH curve.

One of the ways that the titrfacn program can be used in the classroom is to interactively fit experimental titration data. Consider the following experiment. A student is given 50.0 mL of an acetic acid solution of unknown concentration. They titrate this solution with 0.100 M sodium hydroxide, measuring the pH every 10.0 mL using a CBL and a pH probe. The data is given in Table 1 and a plot of this data is shown in Figure 8.

Figure 9 gives the first eight screen shots of the titrfacn.86p program with a guess of 0.100 M for the unknown concentration of the acetic acid. As we can see from the poor

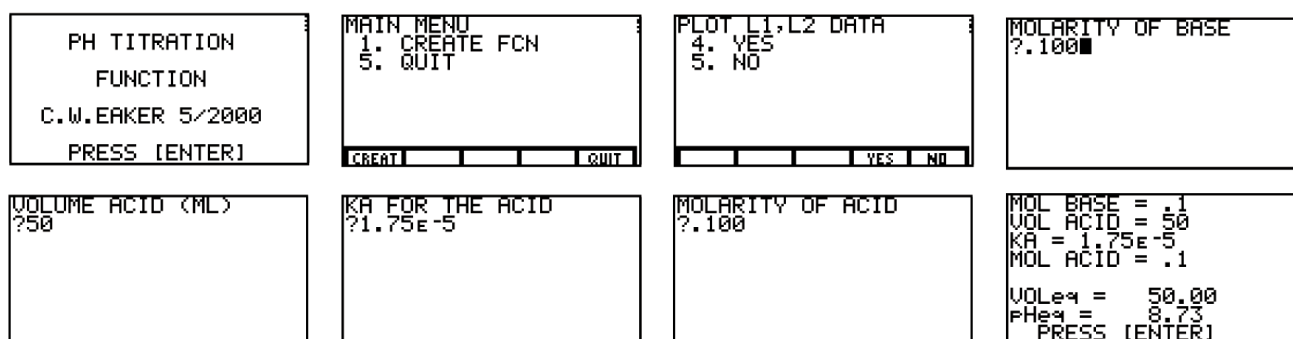


Figure 9. Screen shots showing the input of data into program titrafcn.86p on a TI-86 calculator.

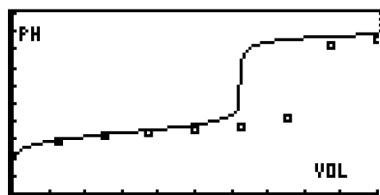


Figure 10. A plot of the pH function using a guess of 0.100 M for the concentration of the unknown acid.

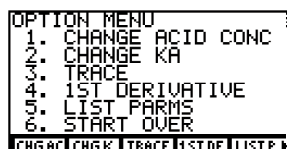


Figure 11. Calculator screen shots showing the second guess of 0.120 M for the concentration of the unknown acid.

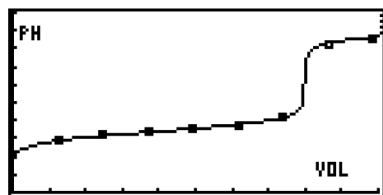
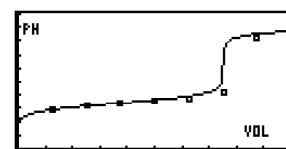
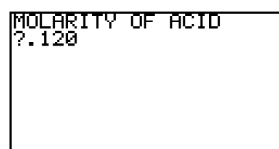


Figure 12. pH titration function with a guess of 0.130 M unknown acid concentration.

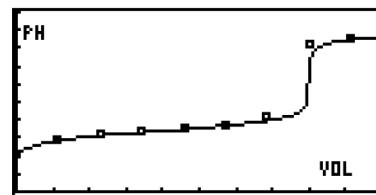


Figure 13. pH titration function with a guess of 0.140 M unknown acid concentration.

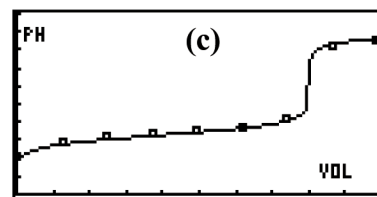
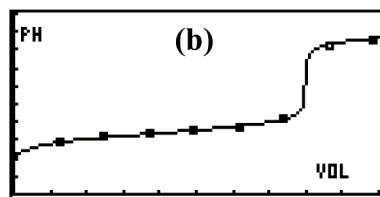
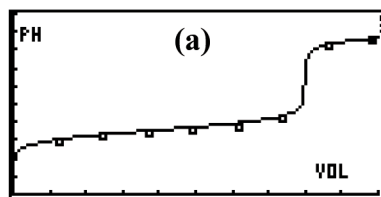


Figure 14. Fit of pH function with (a) $K_A = 1.0 \times 10^{-5}$, (b) $K_A = 1.75 \times 10^{-5}$, and (c) $K_A = 2.5 \times 10^{-5}$. Notice particularly the goodness of the fit in the buffer region.

fit of the data to the equation in Figure 10, the guess of 0.100 M for the unknown concentration is not correct. The graph indicates that the concentration must be larger because the equivalence point occurs at a higher volume of base (further to the right on the VOL axis). Change the concentration guess by choosing option 1 and entering a higher concentration, for example, 0.120 M. This is shown in Figure 11.

We are close to the correct concentration. The results for guesses of 0.130 M and 0.140 M are given in Figures 12 and 13. Clearly, 0.130 M gives the best fit (and is the right answer) to the titration data. One advantage of using this pH-function program is that the experimenter does not need to collect lots of data points, for example, near the equivalence point, to successfully determine the unknown concentration.

Another question we might ask is how sensitive is the pH curve to changes in K_A , the acid ionization constant. In Figure 14 we can see (particularly in the buffer region) the sensitivity of the titration curve to a K_A , which is too small or too large by as little as 0.75×10^{-5} . In Figure 14a, $K_A = 1.0 \times 10^{-5}$ and the pH curve is a little too high and in Figure 14c, $K_A = 2.5 \times 10^{-5}$ and the pH curve is a little below the data points in the buffer region.

The Logistic Function

On the TI-86 (and TI-83) graphing calculator one of the built-in regression equations is for a logistic function,

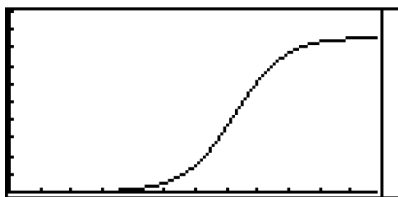


Figure 15. A plot of the logistic function.

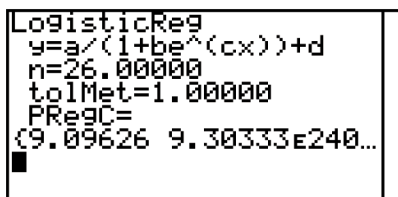


Figure 16. A TI-86 screen shot showing the results of the logistics regression of the strong acid titration data. The parameters are $a = 9.09636$, $b = 9.30333 \times 10240$, $c = 5.55028$, and $d = 2.20962$.

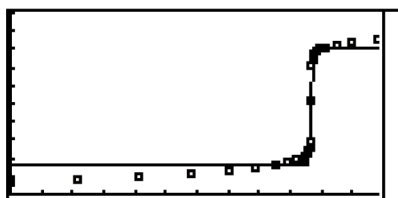


Figure 17. Plot of the strong acid titration data points (boxes) and the logistic regression function (line).

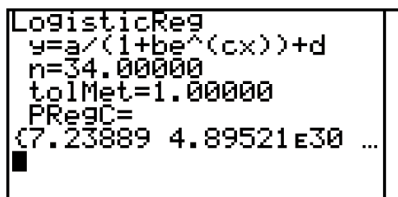


Figure 18. A TI-86 screen shot showing the results of the logistics regression of the strong acid titration data. The parameters are $a = 7.23889$, $b = 4.89521 \times 1030$, $c = 0.70998$, and $d = 4.63091$.

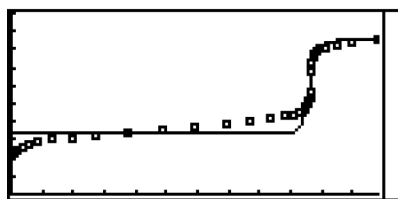


Figure 19. Plot of the weak acid titration data points (boxes) and logistic regression function (line).

$$y(x) = \frac{a}{1 + be^{cx}} + d$$

(for the TI-83 the logistic function has only three parameters, d is set equal to zero). As can be seen in Figure 15 the logistic curve has an S-shape like the titration curve. It has been suggested that this function could be used to model titration data.

Historically, the logistic function is given in the following form

$$y(x) = \frac{\alpha}{(1 + \beta e^{-\kappa x})}$$

It is a general solution of the differential equation

$$\frac{dy}{dx} = \kappa(\alpha - y)y$$

where κ and α are positive constants. This differential equation is attributed to a Belgium mathematician Pierre Verhulst who named it the logistic equation [7]. He proposed this equation to model population growth over time for a population, P , whose growth rate diminishes as $(P_{\infty} - P)$, that is,

$$\frac{dP}{dt} = k(P_{\infty} - P)P$$

(for a population growing exponentially, $dP/dt = kP$) where k is a growth rate constant. With the parameters, $\alpha = 12$, $\beta = 8103$, and $\kappa = 0.01$, the logistic curve is S-shaped (or sigmoid) and looks similar (see Figure 15) to the pH curve we saw earlier. The point of inflection for the logistic curve occurs at $x = (\ln \beta)/\kappa\alpha = 75$ and $y = \alpha/2 = 6$. The slope dy/dx at the point of inflection is $\kappa(\alpha/2)^2 = 0.36$. The logistic curve has only one inflection point and it is symmetric about that point (unlike the pH titration curve).

In biology, the logistic function has been used to successfully model experimental population data. It is also a good model for the spread of an infectious disease through a population. In chemistry, the change in concentration with time for certain autocatalytic reactions has been found to be logistic. Let us now look at how well it models titration curves.

We will use the logistic regression (LGST R L1, L2, Y1 on the TI-86) to fit the strong acid titration data points. This calculation takes about 6 min on the TI-86. The results are shown on Figure 16. The logistic regression for this strong acid titration does not converge on the TI-83 (the value of b exceeds the limit of $9.999... \times 10^{99}$). Figure 17 gives a plot of the logistic regression equation with the data points shown as boxes. The fit is acceptable in the equivalence point region, but it is not very good in the other regions of the graph. Let us use the calculated values of the logistic parameters to determine the x and y values of the inflection point for the logistic function. These should correspond to the volume of base and the pH at the equivalence point.

$$x (= V_{B,eq}) = -\ln(b)/c = 99.968 \text{ mL}$$

$$y (= \text{pH}_{eq}) = (a/2) + d = 6.758$$

These are close to the correct values of 100.0 mL and $\text{pH}_{eq} = 7.00$ for the strong acid titration.

Figures 18 and 19 give the results for the logistic fit of the weak acid titration. This calculation takes about 10 min on the TI-86. (The results on the TI-83 are $a = 7.2401$, $b = 4.657 \times 10^{30}$, $c = -0.7095$ after subtracting 4.63 from the pH values.)

The overall fit is less successful for the weak acid; however, as with the strong acid, the fit in the equivalence region is not too bad. The calculated value of $V_{B, eq} = -\ln(b)/c = 99.5$ mL is close to the correct value of 100.0 mL, and the value of $\text{pH}_{eq} = (a/2) + d = 8.25$ is below the correct value of 8.85.

Conclusions

The pH titration function presented in this article provides a general functional form for representing the change of pH during the titration of strong or weak acids. Students can use this function to analyze pH curves and to determine the unknown concentration of a strong or weak acid. Students can examine how changes in volume, concentration, and equilibrium constants affect the titration curve. Two advantages of this function in comparison to other approximate functions, for example, the logistic function, is that (1) it provides an excellent fit to experimental data with a minimum of effort and (2) the parameters of this function are chemically relevant. One disadvantage of this function is that it is a piecewise function and somewhat complicated. This difficulty can be overcome by using the titrafcn program, which automatically enters the function into the equation editor on the graphing calculator.

Supporting Material

Both programs (titrafcn.86p for the TI-86 and titrafcn.83p for the TI-83) are available in compressed format (single ZIP file) for download at <http://dx.doi.org/10.1007/s00897000426a> or individually at <ftp://chem.udallas.edu/pub/>.

References and Notes

1. de Levie, R. *J. Chem. Educ.* **1993**, *70*, 209–217.
2. de Levie, R. *J. Chem. Educ.* **1999**, *76*, 987–991.
3. Glaister, P. *J. Chem. Educ.* **1999**, *76*, 132.
4. Glaister, P. *J. Chem. Educ.* **1997**, *74*, 760–761.
5. Crippen, K. J.; Mann, R.; Brooks, D. W. *Eightysomething!* **1997** (Spring), 12–13.
6. The programs (titrafcn.86p for the TI-86 and titrafcn.83p for the TI-83) are available for download at the web address <ftp://chem.udallas.edu/pub/> and at *The Chemical Educator* site <http://dx.doi.org/10.1007/s00897000426a>.
7. Redheffer, R. *Introduction to Differential Equations*; Jones and Bartlett Publishers: Boston, 1992.