# The Formalism of Titration Theory

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**Abstract:** Acid–base theory can be rationalized by introducing the concept of the proton function, ${}^{H}C$. Specifically, the pH of any solution is given by ${}^{H}C = 0$, the buffer strength is given by $B = [H^+]d{}^{H}C/d[H^+]$, and the titration of any acid or mixture of acids with a base or mixture of bases (or its inverse) is given by ${}^{H}C_t\, V_t = -{}^{H}C_s V_s$, where t and s denote titrant and sample respectively. The same unifying approach can be extended to complexation, precipitation, and redox equilibria.

## Introduction

Titrations are an important part of classical, "wet" chemistry. The traditional treatment of acid–base titrations follows the typical experimental procedure, in which the pH is measured as a function of the volume of titrant added. Unfortunately, explicit expressions for pH as a function of volume are then obtainable only in the simplest of cases, so that only an approximate, piecemeal approach may be available when explicit expressions are required. Nonetheless, the traditional approach is still used and propagated in the leading textbooks of general and analytical chemistry.

The development of a more modern approach to acid–base titrations apparently started with Hägg's 1940 textbook [1], in which, among other innovations, the progress of a titration was plotted as an explicit function of pH rather than the other way around. Hägg's book has been translated into German [2], and his approach was also used by Scheel [3]. Hägg's general approach to equilibria, including his extensive use of plots of log concentration versus pH, has been popularized in English by an extensive review of Sillén [4] and by an influential book by Butler [5]. Subsequently, Waser [6] showed emphatically that titrations are best treated by considering as dependent variable the extensive parameter titrant volume $V_t$, and as the independent variable the intensive parameter, pH. Willis [7] extended this approach to the titration of mixtures. In our own work, this has now culminated in a fairly general approach [8, 9], for which we will here provide a simple, unifying formalism. In an accompanying communication we have sketched some linear plots that may aid in the understanding of titrations [10].

It is perhaps useful to emphasize here that the actual *measurement* protocol should not be confused with data *interpretation*. In FTIR we measure an interferogram and in FTNMR a free induction decay, yet in both cases we interpret the data in the frequency domain, not in the time domain of their physical measurements. In the same sense, the fact that we measure pH as a function of titration volume does not require that we also interpret the data that way.

Still another issue, pertaining to the specifics of data *analysis*, is whether pH or $V_t$ is the more error-prone, and, therefore, most appropriate as the dependent variable in a least-squares analysis. This depends on the equipment used and on the expertise of the experimenter. In many student titrations with manual burets and commercial pH meters, the errors in $V_t$ dominate, suggesting a plot of $V_t$ versus pH rather than the other way around. But this is a matter of a specific data analysis protocol, somewhat peripheral to the subject of the present communication.

## The Central Property: The Proton Function

The principles of acid–base equilibria are well-known: they are the mass action law of Guldberg and Waage [11, 12] and the conservation of mass and charge. For acid–base problems, the mass and charge balance relations can be combined into a single expression appropriate to acid–base problems, the proton balance. Use of the proton balance (also called proton condition) was promoted especially by Butler [5], and it forms the basis for the present approach.

The proton balance is an equation that lists, on one side, all species that have gained one or more protons (with respect to the starting materials) and, on the other side, all species that have lost one or more protons. This is simply an expression of the requirement that the total number of exchangeable protons must stay constant. The proton balance can often be written down by inspection, and can always be obtained from the mass and charge balance relations. Its usefulness for solving pH problems derives from the fact that it omits the concentrations of any spectator ions (such as the counter-ions of strong acids and bases, for example, $Na^+$ or $Cl^-$) that do not contribute directly to the pH. For example, for a single strong acid such as HCl, we have $[H^+] = [Cl^-] + [OH^-]$; for a single weak acid, HA, we have likewise $[H^+] = [A^-] + [OH^-]$; for a single diprotic acid, $H_2A$, we find $[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$, while the proton balance for a mixture of a monoprotic acid HA and a diprotic weak acid $HA'_2$ reads $[H^+] = [A^-] + [HA'^-] + 2[A'^{2-}] + [OH^-]$. In the above examples the proton balance happens to be identical to the charge balance expression, but this is not always the case.

We now write the proton balance in standard form by moving all terms to the side containing the term $[H^+]$, after which it can be written as ${}^{H}C = 0$. In the above examples, we would write ${}^{H}C = [H^+] - [Cl^-] - [OH^-]$ for a solution of HCl and ${}^{H}C = [H^+] - [A^-] - [OH^-]$ for the solution of a single monoprotic acid; we find ${}^{H}C = [H^+] - [HA^-] - 2[A^{2-}] - [OH^-]$ for a diprotic acid, $H_2A$, and ${}^{H}C = [H^+] - [A^-] - [HA'^-] - 2[A'^{2-}] - [OH^-]$ for a mixture of a monoprotic acid HA, and a

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diprotic weak acid HA′$_2$. We will call $^HC$ the *proton function*. Clearly, the pH can be obtained by expressing $^HC$ explicitly in terms of [H$^+$] and by subsequently solving the resulting expression for $^HC = 0$. In the above examples, we might write $^HC = [H^+] - C - K_w/[H^+] = 0$ for $C$ M HCl, $^HC = [H^+] - K_aC/([H^+]+K_a) - K_w/[H^+] = 0$ for $C$ M HA, $^HC = [H^+] - ([H^+]K_{a1}+2K_{a1}K_{a2})\,C/([H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}) - K_w/[H^+] = 0$ for $C$ M $H_2A$, and $^HC = [H^+] - K_aC_1/([H^+]+K_a) - ([H^+]K_{a1}+2K_{a1}K_{a2})C_2/([H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}) - K_w/[H^+] = 0$ for $C_1$ M HA + $C_2$ M H$_2$A′.

In other words, we will distinguish between the proton balance and the proton function. We will use the term proton balance for the *equation* containing concentrations of proton gainers on one side of the equal sign and the corresponding concentrations of proton losers on the other. We will define the proton function as the *function* we obtain from the proton balance by bringing all concentration terms to one side, such that the concentrations of all proton gainers have positive signs (specifically, the term [H$^+$] should have the coefficient +1), and by then deleting the part that reads = 0. The proton function $^HC$ is, therefore, a sum of concentration terms.

Solving for the pH of a solution is then equivalent to solving

$$^HC = 0 \tag{2}$$

and there are several convenient ways to do so after the proton function has been written as an explicit function of [H$^+$] as indicated above. With a computer one can use a Newton–Raphson or Levenberg–Marquardt [13, 14] algorithm. Alternatively, one can use a logarithmic concentration diagram or stick diagram [8, 9] to visualize what approximations can be made, after which the numerical solution is often obtainable directly or by solving a quadratic expression.

**The Titration**

During a titration, titrant is added to sample. In the resulting mixture neither the proton function $^HC_s$ of the sample nor that of the titrant, $^HC_t$, is zero. Instead, the acid–base titration of a sample of volume $V_s$ with a titrant volume $V_t$ can be described in its entirety by the formally simple expression

$$^HC_t\,V_t = -\,^HC_s\,V_s \tag{3}$$

where $^HC_t$ and $^HC_s$ are the same expressions as those for the pure titrant and sample, respectively (including the terms $C_t$ and $C_s$ that refer to the initial titrant and sample concentrations, i.e., before their mixing), but *at the pH of the sample-plus-titrant mixture*. Alternatively, we can express the titrant volume $V_t$ explicitly as a function of the (fixed) sample volume $V_s$ and the (varying) proton functions of sample and titrant by rewriting eq 3 as $V_t = -\,^HC_sV_s/^HC_t$. As the titration progresses, the pH changes and so do the values of $^HC_s$ and $^HC_t$, because both depend explicitly on [H$^+$].

The numerical evaluation of eq 3 requires that the proton functions $^HC_s$ and $^HC_t$ of sample and titrant, respectively, be expressed explicitly in terms of [H$^+$] and the applicable total analytical concentrations, $C$, and equilibrium constants, $K$. Because $^HC_s$ and $^HC_t$ can be complicated functions of [H$^+$], it is usually much simpler to find $V_t$ as an explicit function of [H$^+$] than it is to express [H$^+$] as a function of $V_t$.

In order to derive eq 3, we consider as sample a mixture of $i$ acids (including acid salts), for which we write

$$^HC_s = [H^+] + \sum_i C_{si}F_{si} - [OH^-] = 0 \tag{4}$$

where the terms $C_i$ represent total analytical concentrations of the components in the sample, while the coefficients $F_i$ contain explicit expressions in terms of the relevant equilibrium constants $K_a$ and [H$^+$]: $F_i = 1$ for a strong monoprotic acid, $F_i = K_a/([H^+]+K_a)$ for HA, $F_i = ([H^+]K_{a1}+2K_{a1}K_{a2})/([H^+]^2 + [H^+]K_{a1}+K_{a1}K_{a2})$ for $H_2A$, $F_i = (-[H^+]^2+K_{a1}K_{a2})/([H^+]^2 + [H^+]K_{a1}+ K_{a1}K_{a2})$ for NaHA, etc. Similarly, we have for the titrant, which in general can be a mixture of $j$ bases (and/or basic salts),

$$^HC_t = [H^+] + \sum_j C_{tj}F_{tj} - [OH^-] = 0 \tag{5}$$

We now recall the origin of these expressions as the charge balance requirement. When we add a titrant volume, $V_t$, to a sample volume, $V_s$, we must consider the resulting mutual dilution of both sample and titrant, that is,

$$[H^+] + \frac{V_s\sum_i C_{si}F_{si}}{V_s+V_t} + \frac{V_t\sum_j C_{tj}F_{tj}}{V_s+V_t} - [OH^-] = 0 \tag{6}$$

or

$$V_s\left([H^+] + \sum_i C_{si}F_{si} - [OH^-]\right) = -V_t\left([H^+] + \sum_j C_{tj}F_{tj} - [OH^-]\right) \tag{7}$$

so that, in view of eqs 4 and 5,

$$\frac{V_t}{V_s} = -\frac{\left([H^+] + \sum_i C_{si}F_{si} - [OH^-]\right)}{\left([H^+] + \sum_j C_{tj}F_{tj} - [OH^-]\right)} = -\frac{^HC_s}{^HC_t} \tag{8}$$

We see that the general relation, eq 3 or 8, simply follows from the *mutual dilution* of sample by titrant, and vice versa.

We certainly don't suggest that a titration merely involves dilution. When we add titrant to a sample, there is of course a chemical reaction, in this case the formation of $H_2O$, and a corresponding change in pH, which will affect the numerical values of the factors $F_i$. The products $C_iF_i$ will determine whether the pH changes at the equivalence points of the titration are large enough to be analytically useful. Regardless of the value of the pH, however, there is mutual dilution of sample and titrant in the reaction vessel, and it is this dilution that leads directly to eqs 3 and 8. In fact we can turn the argument around: a general rule such as eq 3, applicable to all titrations, cannot depend on the particulars of the titration, but must derive from the accounting rules applicable to all titrations, regardless of their analytical usefulness. Microscopic electroneutrality (charge balance) and dilution are indeed such general accounting rules.

At the beginning of the titration we have $V_t = 0$, and eq 3 simply yields ${}^{H}C_s = 0$, the proton function for the sample. (Note that the traditional expression for the part of the titration curve between the onset of the titration and its first equivalence point fails this test.) Similarly, an unlimited excess of titrant would lead to ${}^{H}C_t = 0$, the correct limit for pure titrant.

Incidentally, because only mass and charge balance conditions are used in deriving eq 3, it is not subject to activity effects. Of course, activity coefficients affect the $K_a$ values, and must be used with any experimental values for $[H^+]$ derived from electrometric pH measurements. But the expression for ${}^{H}C$, as written in terms of the concentrations of proton gainers and losers, is simply an accounting of protons and, therefore, does not involve any activity correction.

## The Buffer Strength

The acid buffer strength, $B$, and the corresponding buffer value, $\beta = B/\log e \approx 2.3\ B$, as defined originally by van Slyke [15], can also be related to the proton function. This is not surprising, because both depend only on the acid–base properties of the solution considered and should, therefore, be definable in terms of ${}^{H}C$. For example, for the buffer strength of an acid, we can start from the expression for the progress of its titration with a strong base, and combine it with eq 8 to obtain

$$\begin{aligned} B &= -\ C_a\ [H^+] \left( \frac{d\,(C_b V_b / C_a V_a)}{d[H^+]} \right)_{C_b \to \infty} \\ &= -[H^+] \left( C_b \frac{d\,(V_b/V_a)}{d[H^+]} \right)_{C_b \to \infty} \\ &= [H^+] \left( \frac{C_b}{{}^{H}C_b}\ \frac{d\,{}^{H}C_a}{d[H^+]} \right)_{C_b \to \infty} \\ &= [H^+] \left( \frac{C_b}{{}^{H}C_b} \right)_{C_b \to \infty} \frac{d\,{}^{H}C_a}{d[H^+]} = [H^+]\ \frac{d\,{}^{H}C_a}{d[H^+]} \end{aligned} \tag{9}$$

because ${}^{H}C_b = [H^+] + C_b - [OH^-]$, so that $C_b/{}^{H}C_b$ tends to 1 for $C_b \to \infty$. In general, we have

$$B = \frac{d\,{}^{H}C}{d \ln[H^+]} = [H^+]\ \frac{d\,{}^{H}C}{d[H^+]} \tag{10}$$

and

$$\begin{aligned} \beta &= -\frac{d\,{}^{H}C}{d\mathrm{pH}} = -\frac{d\,{}^{H}C}{d[H^+]} \Big/ \frac{d\mathrm{pH}}{d[H^+]} \\ &= \frac{[H^+]}{\log e}\ \frac{d\,{}^{H}C}{d[H^+]} \approx 2.3\ [H^+]\ \frac{d\,{}^{H}C}{d[H^+]} \end{aligned} \tag{11}$$

## Discussion

The traditional treatment of titration curves considers them as composed of separate points and line segments. For example, in the titration with NaOH of the fully protonated form, $H_6YCl_2$, of ethylene diamine tetraacetic acid, a hexaprotic acid, this would mean seven discrete points (at the beginning of the titration and at each of the six equivalence points) in addition to seven line segments (between the beginning and the first equivalence point, between the first and second equivalence point, and so on till beyond the sixth equivalence point. Moreover, none of those line segments pass through the equivalence points, but instead tend to $-\infty$ or $+\infty$ at the corresponding pH values. Try to fit experimental data to such a monstrosity. Instead of a simple equation (eq 3) representing the entire titration in terms of a single expression, the traditional approach splits that curve into seven points plus seven unconnected, approximate line segments. No wonder that such a piecemeal approach is often considered difficult. Moreover, the entire approach is approximate, but the precise nature of the approximations made is not transparent [16]. And this in a branch of chemistry that usually prides itself on its emphasis on accuracy! In the appendix we show the specific expressions for the titration of $H_6YCl_2$ with NaOH and for the titration of its disodium salt, $Na_2H_2Y$, with either NaOH or HCl.

Before we leave this topic, we want to emphasize that the above approach is by no means restricted to acid–base titrations. The progress of redox titrations [17] and the corresponding redox buffer strength [18] can likewise be described in terms of the corresponding electron conditions, ${}^{E}C$; the progress of complexometric titrations in terms of the corresponding ligand conditions, ${}^{L}C$; etc., assuming that other variables (such as the pH during a redox or complexometric titration) are kept constant by appropriate buffering. In all such cases we can describe titrations simply as

$$n_t{}^{*}C_t V_t = -n_s{}^{*}C_s V_s \tag{12}$$

where ${}^{*}C_t$ and ${}^{*}C_s$ denote the appropriate (proton, electron, ligand, etc.) conditions of the pure titrant and sample respectively, the asterisk being the placeholder for the particular function involved, while $V_s$ is the (fixed) volume of sample titrated and $V_t$ the (varying) volume of titrant added during the titration. The stoichiometric factors $n_t$ and $n_s$ are unity for acid–base problems, which proceed one proton at a time, but are often integers larger than 1 in redox titrations. The minus sign reflects the fact that only one of the two participants in the titration can gain protons (electrons, ligands, etc.), while the other must lose them.

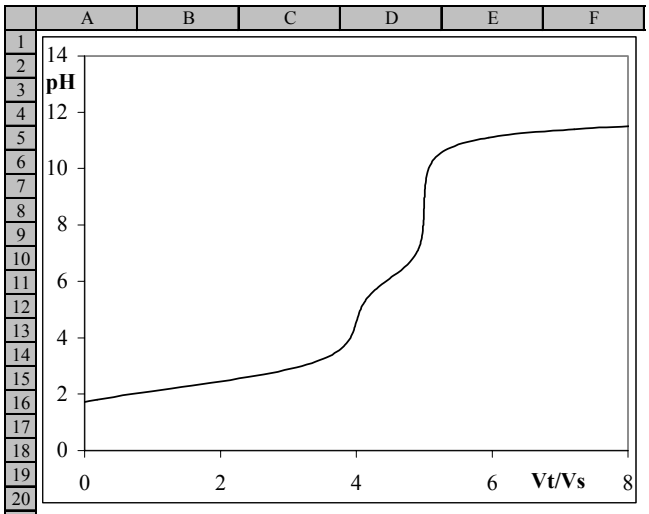
The formal theory of ionic equilibria really cannot get much simpler.

## Appendix

The applicability of the above formalism will be illustrated here for the hexaprotic acid $H_6YCl_2$ and for its disodium salt $Na_2H_2Y$. For a $C_s$ M solution of the fully protonated acid in water the proton function is

$${}^{H}C_s = [H^+] - C_s F_s - K_w/[H^+] \tag{A1}$$

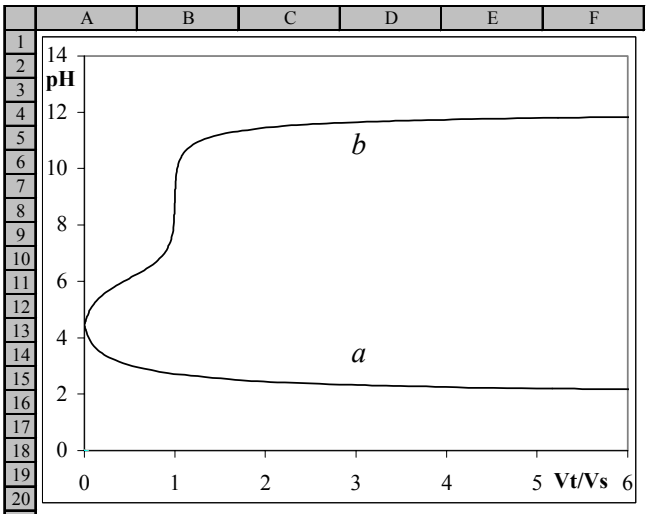
where $F_s$ = numerator/denominator with




| | | | | |
|---|---|---|---|---|
| Cs = 0.01 | Ka1 = 1.00E-01 | Ka4 = 2.09E-03 | | |
| Ct = 0.01 | Ka2 = 3.16E-02 | Ka5 = 7.76E-07 | | |
| Kw = 1.00E-14 | Ka3 = 1.00E-02 | Ka6 = 6.76E-13 | | |

| pH | [H] | num | denom | Vt/Vs |
|---|---|---|---|---|
| 1.7 | 0.020 | 2.18E-09 | 1.16E-09 | -3.84E-02 |
| 1.8 | 0.016 | 9.43E-10 | 4.58E-10 | 1.84E-01 |
| 1.9 | 0.013 | 4.22E-10 | 1.89E-10 | 4.32E-01 |
| 2.0 | 0.010 | 1.95E-10 | 8.09E-11 | 7.03E-01 |
| 2.1 | 0.008 | 9.26E-11 | 3.60E-11 | 9.89E-01 |
| 2.2 | 0.006 | 4.54E-11 | 1.66E-11 | 1.28E+00 |

**Figure 1.** The top of an Excel spreadsheet for the titration of $H_4YCl_2$ with NaOH with columns for pH, $[H^+]$ = 10^–pH; *numerator* and *denominator* as defined in eqs A2 and A3, respectively; and $V_t/V_s = -{}^{H}C_s/{}^{H}C_t$. The titration curve shows that, for the analytical determination of an unknown concentration, the first three equivalence points are analytically useless (because the p$K_a$s are too close together), the fourth is fair, the fifth is good, and the sixth is again useless (as it is too close to that of water). Negative values of $V_t/V_s$ reflect physically unrealizable pH values.




| | | | | |
|---|---|---|---|---|
| Cs = 0.01 | Ka1 = 1.00E-01 | Ka4 = 2.09E-03 | | |
| Ct = 0.01 | Ka2 = 3.16E-02 | Ka5 = 7.76E-07 | | |
| Kw = 1.00E-14 | Ka3 = 1.00E-02 | Ka6 = 6.76E-13 | | |

| pH | [H] | num | denom | Vb/Vs | Va/Vs |
|---|---|---|---|---|---|
| 2.0 | 0.010 | -1.29E-10 | 8.09E-11 | -1.30E+00 | 2.59E+10 |
| 2.1 | 0.008 | -5.15E-11 | 3.60E-11 | -1.24E+00 | 1.08E+01 |
| 2.2 | 0.006 | -2.12E-11 | 1.66E-11 | -1.17E+00 | 5.16E+00 |
| 2.3 | 0.005 | -8.98E-12 | 7.97E-12 | -1.08E+00 | 3.26E+00 |
| 2.4 | 0.004 | -3.90E-12 | 3.94E-12 | -9.93E-01 | 2.31E+00 |
| 2.5 | 0.003 | -1.73E-12 | 2.01E-12 | -8.95E-01 | 1.72E+00 |

**Figure 2.** The top of an Excel spreadsheet for the titrations of $Na_2H_2Y$ with either a strong monoprotic acid (*a*) or a strong monoprotic base (*b*), with columns for pH, $[H^+]$ = 10^–pH, *numerator*′ and *denominator* as defined in eqs A2′ and A3, respectively, and $V_t/V_s = -{}^{H}C_s/{}^{H}C_t$. The titration with a strong acid produces a curve without distinguishing features, of little use for an analytical determination of the concentration of the disodium salt, although its numerical analysis can yield approximate values for the first few p$K_a$s of EDTA. Curve *b* illustrates that titration of the disodium salt of EDTA with NaOH yields a sharp equivalence point, which can be used to determine the salt concentration $C_s$ as well as the value of $K_{a5}$.so that the titration of $C_s'$ M $Na_2H_2Y$ with $C_t$ M NaOH is described by eq 3 plus ${}^{H}C_t = [H^+] + C_t - K_w/[H^+]$, whereas the titration of $C_s'$ M $Na_2H_2Y$ with $C_t$ M HCl is given by eq 3 with ${}^{H}C_t = [H^+] - C_t - K_w/[H^+]$.

$$numerator = [H^+]^5K_{a1}+2[H^+]^4K_{a1}K_{a2} + 3[H^+]^3K_{a1}K_{a2}K_{a3} + 4[H^+]^2K_{a1}K_{a2}K_{a3}K_{a4} + 5[H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + 6[H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6} \quad (A2)$$

and

$$denominator = [H^+]^6+[H^+]^5K_{a1} + [H^+]^4K_{a1}K_{a2} + [H^+]^3K_{a1}K_{a2}K_{a3} + [H^+]^2K_{a1}K_{a2}K_{a3}K_{a4} + [H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + [H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6} \quad (A3)$$

so that the titration of $C_s$ M $H_6Y^{2-}$ with $C_t$ M NaOH is described by eq 3 with the sample proton function ${}^{H}C_s$ as defined in eqs A1 through A3, and ${}^{H}C_t = [H^+] + C_t - K_w/[H^+]$.

For a $C_s'$ M solution of the disodium salt, $Na_2H_2Y$, we have (A1′) with (A2′) and (A3), where now

$$ {}^{H}C_s = [H^+] - C_s' F_s' - K_w/[H^+]$$

$$= [H^+] - C_s' \text{ numerator}'/\text{denominator} - K_w/[H^+] \quad (A1')$$

and

$$numerator' = [H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5} + 2[H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6} - 4[H^+]^6 - 3[H^+]^5K_{a1} - 2[H^+]^4K_{a1}K_{a2} - [H^+]^3K_{a1}K_{a2}K_{a3} \quad (A2')$$

The complexity of eqs A2, A2′, and A3 reflects that of a hexaprotic acid and its salts. Such expressions are most readily evaluated on a spreadsheet or with some other computer program. If the concentrations and equilibrium constants are known, this is a straightforward expression in $[H^+]$ from which the ratio $V_t/V_s$ can readily be computed for any value of $[H^+]$. For fitting experimental data to such a curve, a nonlinear-least-squares Levenberg–Marquardt routine (such as Solver in Excel) can be used with the unknown concentration as the adjustable parameter. (When only one unknown is sought, one could even use a simple Newton–Raphson method.) A nonlinear-least-squares approach can also be used when one or more of the equilibrium constants are unknown. In fact, this is one of the ways to determine the numerical values of such equilibrium constants, directly from titration curves.

Figure 1 illustrates a spreadsheet computation for the titration of the acid and Figure 2 the same for the titration of the salt with either base or acid. Details of how to use Solver to fit experimental data to such a theoretical curve have been described [19].

Apart from dilution effects, which are slightly different for the two situations, one can consider Figure 2 as Figure 1 folded in half starting at $V_t/V_s = 4$ on curve (*a*) of Figure 2, moving towards $V_t/V_s = 0$, and then following curve (*b*) out till $V_t/V_s = 4$.

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