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General Expressions for Acid−Base Titrations of Arbitrary Mixtures

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A single, general master equation is given for acid−base titrations, describing the entire progress of the titration, and equally valid for the titration of a single strong acid with a strong base as for the titration of an arbitrary mixture of acids with an arbitrary mixture of bases, or vice versa.

Acid−base titrations are the backbone of classical quantitative analysis. Initially, color indicators were used to detect their equivalence points, and a rigorous theory for their complete course was neither required nor testable. The advent of pH meters changed that, but the theory did not catch up. Instead, titration curves continued to be described in terms of a number of isolated points (for the onset of the titration, and for each equivalence point), together with approximate intermediate segments not quite connecting those discrete points. While this yields a fairly close approximation for the titration of single, monoprotic acids and bases, it fails for more complicated systems, such as polyprotic acids or bases and their salts, and especially for mixtures of these.

Consequently, for the determination of equilibrium constants from titration curves, special numerical algorithms were developed to fit experimental data. Alternatively, expressions for the various chemical equilibria can be solved by computer as a set of simultaneous equations. While both methods lead to correct numerical results, they are rather nontransparent to the general user and cannot be used in parametric form. In the present work, we develop a simple yet general closed-form expression for acid−base titrations of arbitrary mixtures of monoprotic and polyprotic acids and bases.

Earlier we showed that simple, closed-form solutions describing the progress of a titration can be obtained when the traditional approach of writing the pH (the intensive property) as an explicit function of the volume of titrant used (the extensive property) is abolished in favor of the reverse process.[1] Here we extend this approach to arbitrary mixtures of acids, bases, and salts. The generalization requires only a slight redefinition of the concepts of proton association and dissociation functions.

SIMPLE MIXTURE OF ACIDS

In principle, there are only two considerations. First and foremost, any titration in a macroscopic volume must obey the electroneutrality constraint of such a volume, i.e., the charge balance. Second, because titrant is added to the sample during the titration, modified mass balance relations must be used that specifically take into account the mutual dilution of sample by titrant and vice versa. By combining these, we can formulate an explicit expression for the titrant volume as a function of the hydrogen ion concentration. Below we will first illustrate this approach for the titration with the single strong monoprotic base NaOH of a mixture of the strong monoprotic acid HCl, the weak monoprotic acid HAc, and the weak triprotic acid H_3PO_4. Subsequently, we will proceed directly to the final result for an arbitrary mixture of acids and bases and illustrate some of its applications.

During the titration, we add a volume V_b of the base (in this example, NaOH) of concentration C_b to the fixed sample volume V_a containing the three acids: HCl at a total analytical concentration C_a, HAc at a total analytical concentration C_a', and H_3PO_4 at a total analytical concentration C_a''. We first formulate the mass balance relations. To represent the dilution of the sample as the result of the addition of titrant, we write

$$[Cl^-] = C_aV_a/(V_a + V_b) \quad (1)$$

$$[HAc] + [Ac^-] = C_a'V_a/(V_a + V_b) \quad (2)$$

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = C_a''V_a/(V_a + V_b) \quad (3)$$

Likewise, we have for the dilution of the titrant by the sample

$$[Na^+] = C_bV_b/(V_a + V_b) \quad (4)$$

For acetic acid, we use the concentration fractions α to express $[Ac^-]$ in terms of eq 2, i.e.,

$$\alpha_{Ac^-} = [Ac^-]/\{[HAc] + [Ac^-]\} = K_a'/\{[H^+] + K_a'\} \quad (5)$$

where

$$K_a' = [H^+][Ac^-]/[HAc] \quad (6)$$

and, likewise, for the various phosphate ions,

$$\alpha_{H_3PO_4} = [H_3PO_4]/[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = [H^+]^3/\text{denom} \quad (7)$$

$$\text{denom} = [H^+]^3 + [H^+]^2K_{a1}'' + [H^+]K_{a1}''K_{a2}'' + K_{a1}''K_{a2}''K_{a3}'' \quad (8)$$

(1) de Levie, R. *J. Chem. Educ.* **1992**, *70*, 209.

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$$\alpha_{H_2PO_4^-} = [H^+]^2 K_{a1}''/\text{denom} \quad (9)$$

$$\alpha_{HPO_4^{2-}} = [H^+] K_{a1}'' K_{a2}''/\text{denom} \quad (10)$$

$$\alpha_{PO_4^{3-}} = K_{a1}'' K_{a2}'' K_{a3}''/\text{denom} \quad (11)$$

$$K_{a1}'' = [H^+][H_2PO_4^-]/[H_3PO_4] \quad (12)$$

$$K_{a2}'' = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \quad (13)$$

$$K_{a3}'' = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \quad (14)$$

After all these preliminaries, we introduce the charge balance relation

$$[H^+] + [Na^+] = [Cl^-] + [Ac^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-] \quad (15)$$

into which we substitute the above relations, to obtain

$$C_a V_a + C_a' V_a \alpha_{Ac^-} + C_a'' V_a \{\alpha_{H_2PO_4^-} + 2\alpha_{HPO_4^{2-}} + 3\alpha_{PO_4^{3-}}\} - C_b V_b = \{[H^+] - [OH^-]\}\,(V_a + V_b) \quad (16)$$

Collecting terms in V_b and V_a finally yields the desired expression,

$$\frac{V_b}{V_a} = (C_a + C_a'\alpha_{Ac^-} + C_a''\{\alpha_{H_2PO_4^-} + 2\alpha_{HPO_4^{2-}} + 3\alpha_{PO_4^{3-}}\} - [H^+] + [OH^-])/(C_b + [H^+] - [OH^-])$$

$$= \frac{F_a C_a + F_a' C_a' + F_a'' C_a'' - \Delta}{C_b + \Delta} = \frac{\sum F_a C_a - \Delta}{C_b + \Delta} \quad (17)$$

where

$$\Delta = [H^+] - [OH^-] \quad (18)$$

and the proton dissociation functions F_a are given by

$$F_a = 1 \quad (19)$$

$$F_a' = \alpha_{Ac^-} \quad (20)$$

$$F_a'' = \alpha_{H_2PO_4^-} + 2\alpha_{HPO_4^{2-}} + 3\alpha_{PO_4^{3-}} \quad (21)$$

For a fully dissociated (i.e., strong) acid, the proton dissociation function is 1, as in eq 19. For a polyprotic acid such as orthophosphoric acid, it is equal to the sum of the concentration fractions α, each weighted by the number of protons lost with respect to the starting compound, H_3PO_4. For any polyprotic acid, deleting the valencies for notational simplicity, we have the general expressions

$$F_a = \alpha_{H_{n-1}A} + 2\alpha_{H_{n-2}A} + 3\alpha_{H_{n-3}A} + \ldots + n\alpha_A \quad (22)$$

where

$$\alpha_{H_mA} = \frac{[H]^m K_1 K_2 \ldots K_{n-m}}{[H]^n + [H]^{n-1} K_1 + [H]^{n-2} K_1 K_2 + \ldots + K_1 K_2 \ldots K_n} \quad (23)$$

with $m = 1, 2, \ldots, n$, while

$$K_m = \frac{[H]\,[H_{n-m}A]}{[H_{n-m+1}A]} \quad (24)$$

The simple, additive form of the rightmost expression in eq 17 reflects the analytically useful property that the number of moles of titrant required reflects the *sum* of the number of moles of acids, each weighted by the number of protons involved in their neutralization; an expression of $[H^+]$ in terms of V_b would not be expected to reflect such additivity. This additivity derives directly from the charge balance equation, which is additive in the concentrations of all species present, each weighted by the valency of the species. This additivity is presented in the above formalism by relegating the mathematical complexity of polyprotic equilibria to the proton dissociation functions F_a and, more specifically, to the concentration fractions α.

GENERALIZATION

A similar formalism can be used for weak mono- and polyprotic bases, in which case we can use the proton association function

$$F_b = \alpha_{HB} + 2\alpha_{H_2B} + 3\alpha_{H_3B} + \ldots + n\alpha_{H_nB} \quad (25)$$

which accounts for the fraction of dissociable protons that can be bound to a base B, again deleting valencies. The subscript b denotes the role of a base as a proton acceptor.

In principle, we can titrate an arbitrary mixture of acids with an equally arbitrary mixture of bases. The derivation follows along the lines sketched above, resulting in the general expression

$$\frac{V_b}{V_a} = \frac{\sum F_a C_a - \Delta}{\sum F_b C_b + \Delta} \quad (26)$$

Similarly, for the titration of an arbitrary set of bases with any number of acids, we obtain

$$\frac{V_a}{V_b} = \frac{\sum F_b C_b + \Delta}{\sum F_a C_a - \Delta} \quad (27)$$

Equations 26 and 27 are explicit, general expressions for acid−base titrations of arbitrary mixtures in water. They describe two different procedures, the titration of acids with base, and vice versa, but they are mathematically identical.

A fully protonated acid can only lose protons, and F_a is obviously an appropriate function to use. Likewise, for a fully deprotonated base, F_b would be our first choice. For an acid salt, matters are more ambiguous, because it can, in principle, be titrated as an acid or as a base; it can therefore be described in terms of either possible proton loss or possible proton gain. Fortunately, there is no real problem here, because we always find that $F_a = -F_b$. We can therefore extend the use of F_b to all

species involved in acid−base equilibria. By defining $F = -F_a = F_b$ for each species participating in the titration, we can then condense eqs 26 and 27 into a single general relation in terms of titrant (t) and sample (s) properties,

$$\frac{V_t}{V_s} = -\frac{\sum F_s C_s + \Delta}{\sum F_t C_t + \Delta} \quad (28)$$

Functions similar to F, Fa, and F_b are widely used in the literature, often denoted[2,3] by symbols such as Z or $\bar{n}$. There is, however, a subtle difference with these earlier symbols, because they were usually not tied to the particular species used in the sample and titrant but, instead, to the entire acid−base system considered. This makes them notationally less convenient to use when the sample is a mixture. The same applies to use of the degree of completion of the titration, ϕ.

Below we illustrate the use of F by considering orthophosphoric acid and its sodium and ammonium salts. For H_3PO_4, we have

$$F = F_b = -F_a = -\alpha_{H_2PO_4^-} - 2\alpha_{HPO_4^{2-}} - 3\alpha_{PO_4^{3-}} \quad (29)$$

For the monosodium salt NaH_2PO_4, we have

$$F = F_b = -F_a = -\alpha_{HPO_4^{2-}} - 2\alpha_{PO_4^{3-}} + \alpha_{H_3PO_4} \quad (30)$$

and for $NH_4H_2PO_4$,

$$F = F_b = -F_a = -\alpha_{HPO_4^{2-}} - 2\alpha_{PO_4^{3-}} + \alpha_{H_3PO_4} - \alpha_{NH_3} \quad (31)$$

Likewise, we find for Na_2HPO_4,

$$F = F_b = -F_a = -\alpha_{PO_4^{3-}} + 2\alpha_{H_3PO_4} + \alpha_{H_2PO_4^-} \quad (32)$$

and for $(NH_4)_2HPO_4$,

$$F = F_b = -F_a = -\alpha_{PO_4^{3-}} + 2\alpha_{H_3PO_4} + \alpha_{H_2PO_4^-} - 2\alpha_{NH_3} \quad (33)$$

Finally, for Na_3PO_4, we have

$$F = F_b = -F_a = \alpha_{HPO_4^{2-}} + 2\alpha_{H_2PO_4^-} + 3\alpha_{H_3PO_4} \quad (34)$$

and for $(NH_4)_3PO_4$,

$$F = F_b = -F_a = \alpha_{HPO_4^{2-}} + 2\alpha_{H_2PO_4^-} + 3\alpha_{H_3PO_4} - 3\alpha_{NH_3} \quad (35)$$

For mixtures, each component of a mixture contributes its own F and its own concentration C to the appropriate summation in eq 28, where F and C pertain to the original composition of sample or titrant. Equations 26−28 can be used at any pH in, e.g., a "universal" buffer mixture.

DISCUSSION

The most immediate usefulness of eqs 26−28 lies in the fact that they can readily be applied to any acid−base titration, given the initial composition of sample and titrant. They apply to the titrations of acids, bases, their salts, and arbitrary mixtures of the above, and they allow direct comparison with experimental data. No sophisticated computer programs are needed. Of course, the simple formalism hides the mathematical complexity associated with polyprotic acids and bases, because the specific equilibrium constants enter only in the calculations of the various concentration fractions α which define the F values. However, since these α values can always be expressed directly in terms of $[H^+]$ and the appropriate equilibrium constants, the entire calculation is straightforward and noniterative, the type of computation which can be done, e.g., on a spreadsheet. The availability of a general yet exact solution also makes it easier to verify the validity of approximations used, e.g., to determine the precise locations of equivalence points for complicated samples using Gran[4] and Schwartz[5] plots.

Since the reasoning used is based solely on the validity of the charge balance equation, which itself derives from the electroneutrality requirement for macroscopic volumes, the formalism is completely general. Activity corrections will, of course, affect the various equilibrium constants and will thereby make the functions F weakly dependent on the ionic strength (unless the latter is kept constant) and on any other factors affecting activity coefficients. When activity corrections are needed, iterations become unavoidable, but the calculations can still be made readily, even on a spreadsheet,[6] since the uncertainties inherent in ionic activity coefficients seldom justify more than a single iteration.

The dilution correction used in eqs 1−4 does not take into account any additional dilution from periodic rinsing of the inside of the titration vessel. Such additional dilution, noninherent in the titration, can of course be taken into account, at some additional complexity, but only when the volumes of rinse solution used and the pH at which they were added are known. This unnecessary complication is, therefore, best avoided when quantitative data are desired.

Equations 26−28 indicate at precisely what level the titration curve of a mixture of acids or bases is additive in the components of that mixture, something a numerical simulation cannot do. It also provides an interesting link with the proton condition often used in equilibrium pH calculations. For example, at the onset of a titration, before any titrant has been added, V_t in eq 28 must be zero, so that the same must also apply to $\sum F_s C_s + \Delta$. Inspection of $\sum F_s C_s + \Delta = 0$ shows that it is, indeed, the proton condition for the sample, written in standard form, i.e., with all its parameters on the left-hand side. Likewise, $\sum F_t C_t + \Delta = 0$ is the proton condition for the titrant. Similar considerations apply to eqs 26 and 27.

The quantities $\sum F_s C_s + \Delta$ and $\sum F_t C_t + \Delta$ appearing on the right-hand side of eq 28 implicity depend on $[H^+]$, both through Δ and, for weak acids and bases, through the functions F. At the beginning of the titration, V_t is zero, and so is $\sum F_s C_s + \Delta$, which

(2) Sillén, L. G. In *Treatise on Analytical Chemistry*; Kolthoff, I. M., Elving, P. J., Eds.; Interscience: New York, 1959; Vol. I, Part 1, p 277.
(3) Rossotti, F. J.; Rosotti, H. *The Determination of Stability Constants in Solution*; McGraw-Hill: New York, 1961.
(4) Gran, G. *Analyst* **1952**, *77*, 661.
(5) Schwartz, L. M. *J. Chem. Educ.* **1987**, *64*, 947.
(6) de Levie, R. *A Spreadsheet Workbook for Quantitative Chemical Analysis*; McGraw-Hill: New York, 1992; p 11-6.

one can use to compute the pH of the sample. When the titration is continued far beyond its equivalence point(s), V_t/V_s will tend to infinity, and $\sum F_t C_t + \Delta$ will approach zero; from $\sum F_t C_t + \Delta = 0$, we can find the pH of the titrant. During the progress of the titration, $[H^+]$ assumes values intermediate between these two extremes, making neither $\sum F_s C_s + \Delta$ nor $\sum F_t C_t + \Delta$ zero; in this range, V_t/V_s will assume finite, positive values.

The model presented here extends our earlier formalism[1] in a way that is more conducive to treating mixtures. A similar approach can be applied to redox titrations,[7] in which case we have

$$\frac{V_t}{V_s} = -\frac{\sum F_s C_s}{\sum F_t C_t} \tag{36}$$

where F now accounts for electrons gained rather than protons. (The absence of a term equivalent to Δ stems from the fact that, for good reasons, the oxidation and reduction of the solvent are neglected in such models.) This extension makes it possible to calculate the redox titration curves of arbitrary mixtures of oxidizable or reducible species, provided that such curves can be described in terms of equilibrium parameters. Again, a simple formalism is possible for mixtures, where it was earlier believed,[8] even for the titration of a single redox system, that the stoichiometric complexity of redox reactions is such that the meaning of generalized relations for redox titration curves is lost in algebra. As eq 36 shows, this need not be the case.

So far, we have shown that one can use the formalism developed here to calculate the titrant volume V_t as a function of pH. There are, however, numerous instances where one may want to find the pH given the volume of titrant added. Since this is merely the inverse problem, it is simply solved by using a Newton−Raphson approach, which is quite stable since the relation between V_t and $[H^+]$ is both single-valued and monotonic. On modern spreadsheets, Newton−Raphson routines are built in. Thus, there is no more need to sove such problems using differential equation solvers or other computational "black boxes".

Finally, we use three examples to illustrate the usefulness of the present approach. The first merely shows how some analytical problems can be answered much more directly when one calculates the titrant volume V_t as a function of pH rather than the other way around. Likewise, the second and third examples illustrate the rather minimal effort needed for the calculation of the titration curves of rather complex mixtures when using the approach presented here.

Example 1: Titration Error. The estimation of the titration error is a typical analytical problem. For example, given the acid−base equilibrium constants, one may want to estimate the likely error associated with the range over which an indicator changes its color. The pH limits of the color range have been tabulated, and one merely needs to calculate the corresponding titrant volumes. We note that this corresponds to our approach, in that specific pH values (here, the extremes of the pH range of the indicator) are given, and the corresponding titrant volumes must be computed. Therefore, the calculation is straightforward: one selects the pH extremes of the indicator range, calculates V_t/V_s for these limits, and determines the resulting titration error as the difference between this and the equivalence point value of V_t/V_s. Similarly, for a potentiometric titration, the titration error resulting from any presumed or anticipated reading error ΔpH can be obtained immediately.

Table 1. Estimates of the Range in V_b/V_a Corresponding to the Listed Transition Ranges[10] of the Color Indicators Shown, for the Titration of 10 mM Acetic Acid ($pK_a = 4.76$) with 10 mM NaOH at 25 °C ($pK_w = 14.00$)

indicator	pH range	V_b/V_a range (%)
cresol red	7.2−8.8	−0.36 to +0.12
α-naphtholphthalein	7.3−8.7	−0.28 to +0.09
cresol purple	7.4−9.0	−0.22 to +0.19
thymol blue	8.0−9.6	−0.04 to +0.80
phenolphthalein	8.2−10.0	−0.00 to +2.02

For our illustration, we calculate the titration error associated with the use of different color indicators in the titration of 10 mM acetic acid with 10 mM NaOH, using the transition ranges listed by Bányai.[9] Taking the pK_a of acetic acid as 4.76, we calculate the pH at the equivalence point as 8.23, and therefore select as possible indicators cresol red (with a pH transition range given[9] as 7.2−8.8), α-naphtholphthalein (listed range 7.3−8.7), cresol purple (range 7.4−9.0), thymol blue (range 8.0−9.6), and phenolphthalein (range 8.2−10.0). Consequently, we merely calculate V_b/V_a for the corresponding values of $[H^+]$. For example, for pH = 7.2, we have $[H^+] = 6.31 \times 10^{-8}$ M, so that eq 5 yields $\alpha_{A^-} = 0.9964$, and V_b/V_a is obtained from eq 26, applied to a single monoprotic weak acid, as 0.9964. For pH = 8.8, we likewise find $V_b/V_a = 1.0012$, so that the pH transition range of cresol red leads to a range of values of from −0.36% to +0.12% around the equivalence point value, $V_b/V_a = C_b/C_a = 1.0000$. Table 1 lists the corresponding error ranges similarly calculated for the above indicators; the computation is so simple that it can easily be performed for a number of indicators, even on a pocket calculator, thereby enabling the analyst to make a rational, optimal choice of available indicators. In the present example, cresol red, α-naphtholphthalein, or cresol purple would make satisfactory indicators, while use of phenolphthalein would not be recommended.

This conclusion is, of course, no better than the numerical data on which it is based. Insofar as the pH transition ranges are estimates for usually undefined ionic strengths, and the pK_a is a value extrapolated to infinite dilution, conclusions from theoretical computations are always subject to experimental verification. However, the point of the present example is to illustrate that the present approach makes it quite easy to obtain numerical estimates of the likely titration errors, starting from measured data, whatever their inherent limitations.

Example 2: Universal Buffer for Use with Metal Cations. A "universal" buffer mixture contains acids chosen such that, over a considerable pH range, the pH is an approximately linear functions of the volume of base added. The pK_a values of the components of universal buffer mixtures often lie quite close together, a situation that causes great difficulties in the traditional, mathematical description of the resulting titration curves. The

(7) de Levie, R. *J. Electroanal. Chem.* **1992**, *323*, 347.
(8) Lingane, J. J. *Electroanalytical Chemistry*; Interscience: New York, 1958; p 135.
(9) Bányai, E. In *Indicators*; Bishop, E., Ed.; Pergamon Press: Oxford, 1972; p 65.

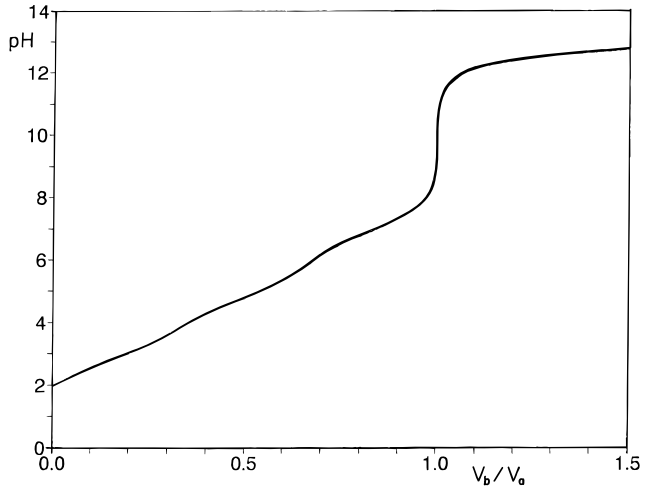

Figure 1. Titration with 0.3 M aqueous NaOH of an aqueous solution containing 0.1 M 3-nitro-2,6-dimethylpyridine ($pK_a = 2.87$) + 0.1 M 2,6-dimethylpyridine-3-sulfonic acid ($pK_a = 4.80$) + 0.1 M 2,6-dimethylpyridine ($pK_a = 6.96$), calculated as explained in the text.

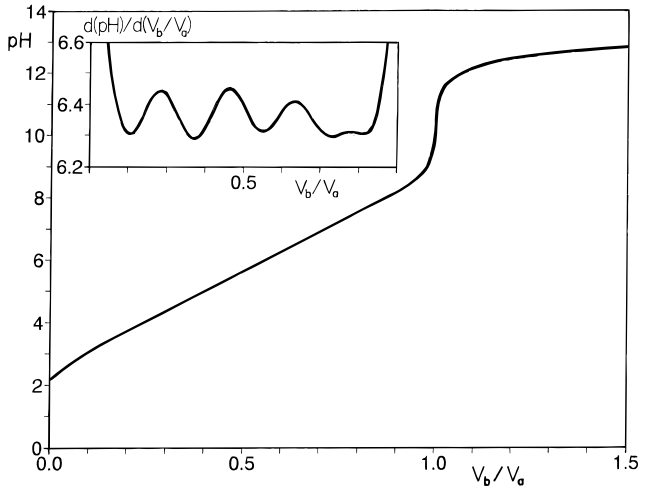

Figure 2. Titration curve calculated for the titration with 0.3 M aqueous NaOH of an aqueous solution containing 0.034 M 3-nitro-2,6-dimethylpyridine ($pK_a = 2.87$) + 0.051 M 4-cyano-2,6-dimethylpyridine ($pK_a = 3.68$) + 0.053 M 2,6-dimethylpyridine-3-sulfonic acid ($pK_a = 4.80$) + 0.051 M 3-acetyl-2,4,6-trimethylpyridine ($pK_a = 5.91$) + 0.048 M 2,6-dimethylpyridine ($pK_a = 6.96$) + 0.063 M 4-methoxy-2,6-dimethylpyridine ($pK_a = 8.04$). Inset: the derivative d(pH)/d(V_b/V_a) versus V_b/V_a, calculated using a moving five-point quadratic,[1] showing that this derivative is constant to within ±1.5% for $0.15 \leq V_b/V_a \leq 0.85$.

formalism given here does not suffer from such complications and is well suited for such calculations, which can readily be performed on, e.g., a simple spreadsheet.

Many proposed universal buffer mixtures contain anions known to form complexes with a variety of metal cations and are therefore of rather limited usefulness for inorganic studies. Bips et al.[10] described a series of buffers based on 2,6-dimethylpyridines that show very limited affinity for many commonly used cations, including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}. Here, we will illustrate the ease of calculating the resulting titration curve by considering two such buffer mixtures. The first is composed of an equimolar mixture of three components: 3-nitro-2,6-dimethylpyridine ($pK_a = 2.87$), 2,6-dimethylpyridine-3-sulfonic acid ($pK_a = 4.80$), and 2,6-dimethylpyridine ($pK_a = 6.96$).

In this case, we can use eq 17, where, for each component, F_a is simply given by eq 5 as $F_a = \alpha_{A^-} = K_a/([H^+] + K_a)$; the individual K_a values follow immediately from the listed pK_a values. The resulting curve for the titration with 0.3 M NaOH of a mixture containing all three components at concentrations of 0.1 M is then described by eq 17, with

$$\sum F_a C_a = \frac{0.1 \times 10^{-2.87}}{[H^+] + 10^{-2.87}} + \frac{0.1 \times 10^{-4.80}}{[H^+] + 10^{-4.80}} + \frac{0.1 \times 10^{-6.96}}{[H^+] + 10^{-6.96}} \quad (37)$$

The titration curve is shown in Figure 1.

When a more nearly linear titration curve is desired, two components with intermediate pK_a values can be included in the mixture. Moreover, the range can be extended somewhat by incorporating yet another component. The resulting mixture might then contain, in addition to the three components already mentioned, 4-cyano-2,6-dimethylpyridine ($pK_a = 3.68$), 3-acetyl-2,4,6-trimethylpyridine ($pK_a = 5.91$), and 4-methoxy-2,6-dimethylpyridine ($pK_a = 8.04$). Again, the calculation of the corresponding progress curve is straightforward. By slightly adjusting the concentrations of the various components (while still, in this example, keeping the total concentration constant at 0.3 M), we can then make the pH a linear function of V_b in the range $3.4 \leq pH \leq 8.1$ to much better than ±0.01 pH, as shown in Figure 2. Again, the ease of calculating the titration curve of the mixture makes it practical to fine-tune the concentrations of the various sample components in order to make a nearly linear titration curve.

Example 3: Titration of a Diprotic Acid with a Mixture of Bases. While the above examples only involved monoprotic acid−base equilibria, our last example illustrates the use of polyprotic acids and bases. Moreover, even though one will seldom intentionally select a mixture as titrant, it can happen anyway. Below, we therefore indicate how to describe the titration of sulfuric acid with sodium hydroxide contaminated with a relatively small amount of carbonate.

For sulfuric acid, we use[12] $pK_{a1} \ll 0$ and $pK_{a2} = 1.99$. In the calculation, we can select any sufficiently large value for K_a, such as 10^{10}, so that

$$F_a = \frac{[H^+]K_{a1} + 2K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \frac{10^{10}[H^+] + 2 \times 10^{10}(10^{-1.99})}{[H^+]^2 + 10^{10}[H^+] + 10^{10}(10^{-1.99})} \quad (38)$$

We can avoid the inelegant use of such an arbitrary value for K_{a1} as follows. Given that $[H^+]$ and K_{a2} are of the order of 1 or less, while K_{a1} is much larger than 1, we rewrite eq 38 as

(10) Bips, U.; Elias, H.; Hauröder, M.; Kleinhans, G.; Pfeifer, S.; Wannowius, K. J. *Inorg. Chem.* **1983**, *22*, 3862.

(11) Savitzky, A.; Golay, M. *Anal. Chem.* **1964**, *36*, 1627.

(12) Smith, R. M.; Martell, A. E. *Critical stability constants*, Vol. 4; Plenum: New York, 1976.

$$F_a = \frac{[H^+]K_{a1} + 2K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \frac{[H^+] + 2K_{a2}}{[H^+]^2/K_{a1} + [H^+] + K_{a2}}$$

$$\approx \frac{[H^+] + 2K_{a2}}{[H^+] + K_{a2}} = 1 + \frac{K_{a2}}{[H^+] + K_{a2}} = 1 + \frac{10^{-1.99}}{[H^+] + 10^{-1.99}} \quad (39)$$

as expected for a strong monoprotic acid plus a weak monoprotic acid.

For sodium carbonate, with $pK_{a1} = 6.35$ and $pK_{a2} = 10.33$,[12] we have

$$F_b = \frac{2[H^+]^2 + [H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \frac{2[H^+]^2 + 10^{-6.35}[H^+]}{[H^+]^2 + 10^{-6.35}[H^+] + 10^{-6.35}(10^{-10.33})} \quad (40)$$

Finally, using the value $K_w = 10^{-14.00}$ for the ion product of water, we obtain the complete expression for the progress of the titration of 0.1 M H_2SO_4 with a mixture of 0.09 M NaOH + 0.005 M Na_2CO_3 as

$$\frac{V_b}{V_a} = [0.1\ \{1 + 10^{-1.99}/([H^+] + 10^{-1.99})\} - \{[H^+] - 10^{-14.00}/[H^+]\}]/[0.09 + (0.005\{2[H^+]^2 + 10^{-6.35}[H^+]\})/([H^+]^2 + 10^{-6.35}[H^+] + 10^{-6.35}(10^{-10.33})) + \{[H^+] - 10^{-14.00}/[H^+]\}] \quad (41)$$

as shown in Figure 3, and its inverse (for titrating the base mixture with the acid) in Figure 4. By now it will be obvious to the reader, even without invoking the (equally straightforward) example of, e.g., a hexaprotic acid such as EDTA, that the conversion of a relation of the type of eq 41 in order to express $[H^+]$ as an explicit function of V_b is usually a hopeless undertaking, whereas the direct calculation of V_b based on an equation such as eq 41 is direct and uncomplicated.

The explicit representation of complicated chemical systems unavoidably leads to complicated equations, a direct consequence of the many equilibria that must be taken into account. Nonetheless, the general structure of the explicit expression for the progress curve remains simple: it is, at worst, the ratio of two sums of ratios. It is gratifying that a single master equation can represent all acid−base titrations, including arbitrary acid and base mixtures, in their entirety and that it is simple enough to be amenable to direct, noniterative evaluation on a spreadsheet.

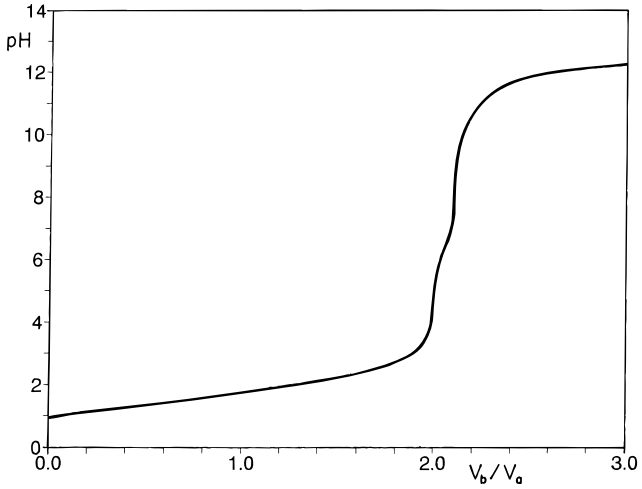

Figure 3. Titration curve, calculated from eq 41, for the titration of 0.1 M H_2SO_4 with a solution containing 0.09 M NaOH + 0.005 M Na_2CO_3.

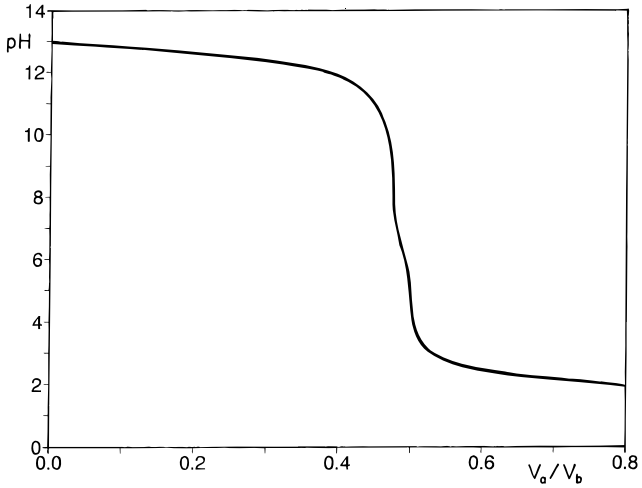

Figure 4. Titration curve for the reverse titration, i.e., of a sample containing 0.09 M NaOH + 0.005 M Na_2CO_3 with 0.1 M H_2SO_4, simply calculated as $V_a/V_b = 1/(V_b/V_a)$, where V_b/V_a is given by eq 41.

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