Analytica Chimica Acta, 206 (1988) 111–123
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

EQUIVALENCE VOLUMES IN POTENTIOMETRIC TITRATIONS[a]

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(Received 9th September 1987)

SUMMARY

The development of methods for finding the equivalence volume by using linear regression methods is reviewed. The methods discussed are mainly those developed and used at the Department of Analytical Chemistry at the Royal Institute of Technology in Stockholm. No attempt has been made to cover the large number of methods of finding the equivalence volume in potentiometric titrations developed elsewhere.

When a titration is done, the aim is to have a compound in the sample solution react in a well defined manner with some other compound in the titrant added. The reactions are the same whether they are followed potentiometrically by inserting an electrode system in the sample solution or some predetermined reaction condition is indicated by the use of a suitable indicator.

In the "good old days", when 100–200 ml of sample solution was titrated with 10–25 ml of titrant from a burette graduated at 0.1-ml intervals, the endpoint, i.e., the equivalence volume, could in most cases be indicated by the shift in the indicator colour for an addition of one drop (about 0.05 ml) of titrant. This was equal to an accuracy or at least a precision of 99.5–99.8%, a figure to be kept in mind when the accuracy or precision of potentiometric titrations is discussed.

TITRATION EQUATIONS AND CURVES

A titration equation is a mathematical expression which more or less realistically describes the relation between the volume of titrant added and the concentration of the ion to be indicated by the indicator electrode. The titra-

[a]This paper was presented at the International Symposium on Titration Techniques held on June 12–15, 1987 in Lund, Sweden.

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tion equation has to include stability and other constants. In order to be able to calculate the equivalence volume from a series of potential values E_i or pH_i versus volume of titrant added, V_i, a suitable titration equation has to be defined, in which not only the main reaction but also at least the important side-reactions are considered. When the titration equation has been set up, it may be possible to see whether some terms can be neglected, at least for some part of the titration, in order to simplify calculations. This was especially important 30–35 years ago, when no electronic calculators were available. As an example, it may be mentioned that in titrations of an acid with a strong base, the term [OH] can be neglected for pH values lower than about 6–8 depending on the concentration and the stability constant of the acid.

A titration equation is monotonous, i.e., it has no maximum or minimum points. Thus the slope dE/dV or dpH/dV is either positive or negative throughout the whole titration; it never shifts sign. The titration curve in a practical titration can be represented by a table of values for E_i or pH_i and V_i, where $i=0$ indicates the start of the titration before any titrant addition. The titration curve can also be a plot of E_i or pH_i versus V_i.

The differential method

If the titration curve is very steep as in Fig. 1, and if many readings are taken in the region of highest slope, the equivalence volume is easily evaluated directly from the readings or the plotted curve in about the same way as when an indicator is used. If the range of the highest slope is less pronounced than in Fig. 1, the so-called differential method or peak curve is often resorted to. Here $\Delta E/\Delta V=(E_{i+1}-E_i)/(V_{i+1}-V_i)$ or $\Delta pH/\Delta V=(pH_{i+1}-pH_i)/(V_{i+1}-V_i)$ is plotted versus $(V_{i+1}+V_i)/2$. Such a peak curve is shown in Fig. 2, where it seems that the maximum is very close to the equivalence volume V_e. The sample was an acid with $\log K_a=7$ titrated with a strong base with a concentration of 0.01 mol l^{-1} in a synthetic titration. However, if the acid is still weaker, log

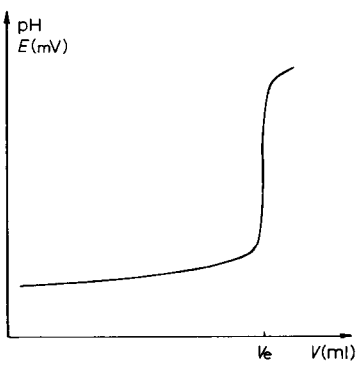

Fig. 1. The equivalence volume, V_e, can be evaluated from the simple titration curve at the point of highest slope.

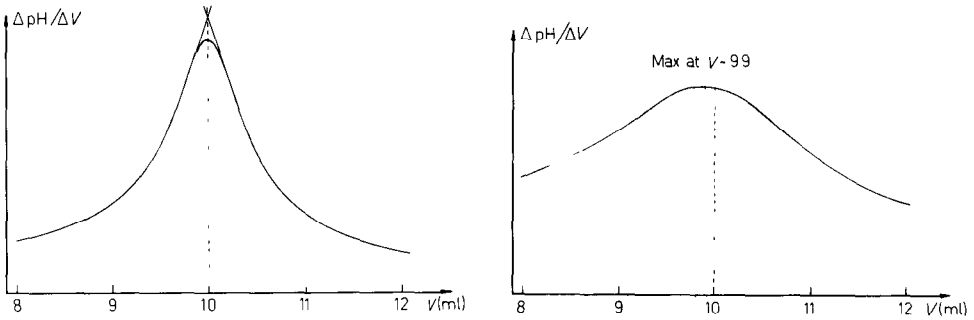

Fig. 2. Peak curve by the differential method, from which V_e can be evaluated reasonably well. Conditions: $C_b = 0.01$ mol l^{-1}, $V_0 = 100$ ml, $V_e = 10.0$ ml; $\log K_a = 7$, $\log K_w = -13.6$.

Fig. 3. Peak curve for a very weak acid; V_e will be inaccurate by about 1%. Conditions: $C_b = 0.01$ mol l^{-1}, $V_0 = 100$ ml, $V_e = 10.0$ ml; $\log K_a = 8$; $\log K_w = -13.6$.

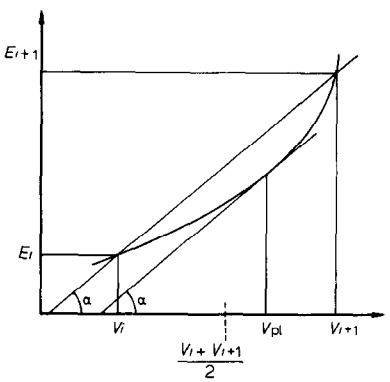

Fig. 4. $\Delta E/\Delta V$ or $\Delta V/\Delta E$ should be plotted at $V = V_{pl}$, not at $V = (V_{i+1} + V_i)/2$.

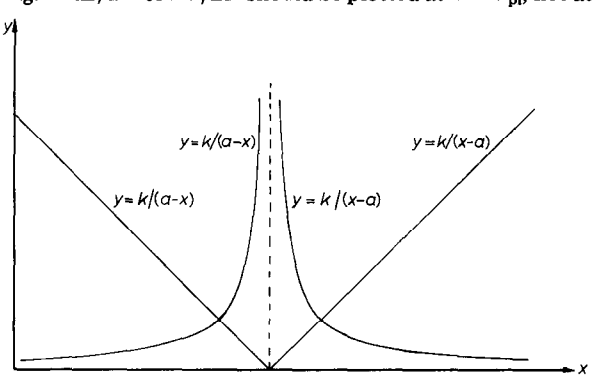

Fig. 5. Inverting the right side of the equation for a hyperbola leads to the equation for a straight line.

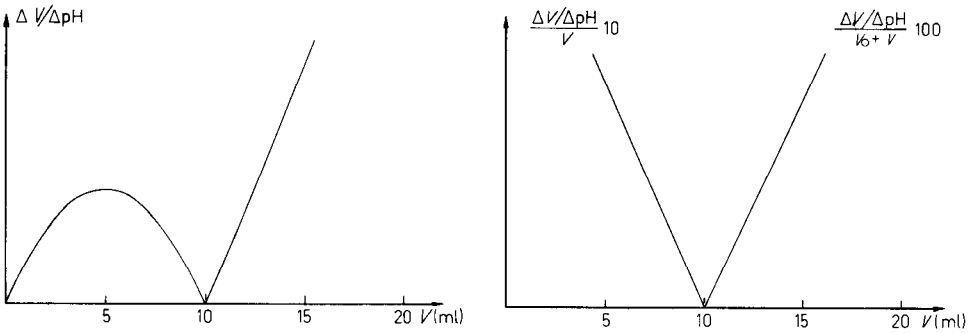

Fig. 6. Inverted peak curve for the titration of a weak acid. Conditions: $C_b = 0.1$ mol l^{-1}, $\log K_a = 6$; otherwise as for Fig. 3.

Fig. 7. Gran I plot of the same titration as in Fig. 6.

$K_a = 8$, the peak curve is as shown in Fig. 3. Here it is seen, first, that the maximum is very flat, which makes it difficult to decide exactly where it is situated; secondly, a closer inspection shows that the maximum is in fact at about $V = 9.9$ ml and not at the theoretical value $V_e = 10$ ml.

The peak curve method is based on no theoretical background other than that the equivalence volume should be the volume where the titration curve has its highest slope, which as seen in Fig. 3 is not always the truth. Another objection to the peak curve is that $\Delta E/\Delta V$ or ΔpH$/\Delta V$ should not be plotted versus $(V_{i+1} + V_i)/2$ but at a volume V_{pl} a little closer to the equivalence volume as shown in Fig. 4. A further limitation is that the peak curve is more or less useless in cases when a stepwise addition of equal volumes of titrant is used in the titration, as the peak curve requires a number of closely spaced titration points close to the equivalence volume.

Inverted peak curve

At least in a first approximation, the two branches of the peak curve look very much like branches of hyperbolas. Now, if the right side of the equation, $Y = k_1/(a - X)$, for a hyperbola is inverted, the equation becomes $Y = k_2(a - X)$, which is the equation for a straight line (Fig. 5).

In 1949, this gave me the idea of plotting $\Delta V/\Delta E$ instead of $\Delta E/\Delta V$ versus V. This resulted in curves of the type shown in Fig. 6, where at least the right branch of the curve is fairly straight. It also showed that the equivalence volume could be found quite accurately from the graph.

THE GRAN I METHOD

Given the possibilities of the inverted peak curve, the functions $dV/$dpH and dV/dE were investigated for a number of titration equations, which in many

cases were rather approximate. Even when these sometimes approximate equations were used, however, it could be shown that in titrations of strong acids

$$(dV/dpH)/(V_0+V) = [\ln 10/V_0+V_e)]\ (V_e-V) \quad (1)$$

and in titrations of at least some types of weak acids

$$(dV/dpH)/V = (\ln 10/V_e)\ (V_e-V) \quad (2)$$

before the equivalence volume. After the equivalence volume

$$(dV/dpH)/(V_0+V) = [\ln 10/(V_0+V_e)]\ (V-V_e) \quad (3)$$

If E is measured instead of pH, Eqn. 1 will be changed to

$$(dV/dE)/(V_0+V) = (1/Q)\ [\ln 10/(V_0+V_e)]\ (V_e-V) \quad (1A)$$

where $Q = RT \ln 10/F$.

With minor approximations (dV/dpH) and dV/dE could be approximated by $\Delta V/\Delta pH$ and $\Delta V/\Delta E$, respectively. By using these expressions, the curved lines in Fig. 6 were transformed to the two straight lines in Fig. 7.

In some cases, like the one shown in Fig. 7, the approximate titration equations yielded quite good straight lines, but in other cases, as in Fig. 8, the approximations used led to excessive uncertainty in locating the equivalence volume.

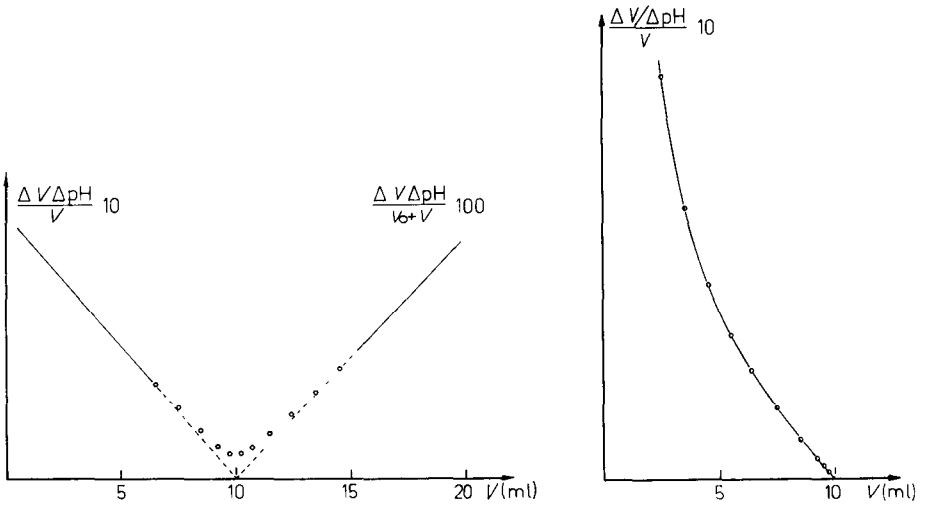

Fig. 8. Gran I plot of the same titration of the very weak acid as in Fig. 3.

Fig. 9. Gran I plot of a weak acid of intermediate strength in which V_e could be found quite accurately by plotting. Conditions: $C_b = 0.1$ mol l^{-1}, $V_0 = 100$ ml, $V_e = 10.0$ ml; log $K_a = 3$, log $K_w = 13.6$.

The Gran **I** method [1] was published in 1950 at a time when electronic calculators were not available and calculations had to be made by slide-rules or mechanical calculating machines, which could only divide and multiply. This is one reason why at that time no more complete titration equations were used and why the equivalence volume was normally found by plotting. In this case, it did not matter very much if the points did not yield a completely straight line as in Fig. 9. Plotting was used also because without electronic calculators it was quite time-consuming to fit even a straight line to a number of points by the method of least squares.

Thus the Gran **I** method suffers from being based on titration equations, which in some cases were too approximate. It also suffers from the same difficulties of choosing the value V_{pl} at which to plot the differential expressions as the peak curve (Fig. 4). However, the method also had a special advantage. In neutralization titrations, the slope of the straight lines should be $\pm(\ln 10)/(V_0+V_e)$ or $\pm(\ln 10)/V_e$ and $\pm(\ln 10)/[Q(V_0+V_e)]$ or $\pm(\ln 10)/(Q V_e)$. This has been used in a slightly modified form to test the electrode response of ion-selective electrodes [2].

THE GRAN II METHOD

Partly based on a method published in 1951 by Sørensen [3], another method, usually referred to as Gran **II**, was developed and published in 1952 [4].

The idea behind this method is the relationships
$\mathrm{ph} = -\log[\mathrm{H}]$ and $[\mathrm{H}] = \text{antilog}(-\mathrm{ph}) = 10^{-\mathrm{ph}}$
where [H] is the hydrogen ion concentration used in a titration equation. As an example, for a strong acid titrated with a strong base

$$[\mathrm{H}] = C_b\,(V_e - V)/(V_0 + V) + [\mathrm{OH}] \tag{4}$$

where C_b is the concentration of the titrant. If [OH] is neglected, then before the equivalence volume

$$(V_0 + V)\,10^{-\mathrm{ph}} = C_b(V_e - V) \tag{5}$$

For calculation purposes, this equation can be written

$$(V_0 + V)\,10^{a-\mathrm{ph}} = b\,(V_e - V) \tag{6}$$

where a and b are constants. Here a can be chosen arbitrarily, e.g., 4, 5 or 6 in the case of a strong acid. If $(V_0+V_i)\,10^{a-\mathrm{ph}}$ is plotted versus V_i, a straight line is obtained which intersects the V-axis at $V=V_e$.

Starting from fairly approximate titration equations, expressions similar to Eqn. 6 were deduced for titrations of weak acids and also for other types of titrations such as precipitation, compleximetric and redox titrations.

Especially the use of the Gran **II** method in acidimetric titrations seems to have aroused a lot of interest and numerous modifications have been proposed,

as it is obvious (e.g., from Fig. 10) that using formulae based on approximate titration equations leads to plots which may deviate quite a lot from straight lines. In this case, the equivalence volume can be read quite accurately from the plot, but the points do not lend themselves to fitting a straight line by numerical methods.

Pehrsson et al. [5] investigated the Gran **II** functions, especially for acidimetric titrations, and found that the range of stability constants of the acids within which the functions could be applied with advantage was in fact rather narrow. This investigation was based on the use of stepwise addition of equal portions of the titrant. Further, no plotting was used by them, but instead straight lines were fitted to the data pairs obtained from the Gran **II** expressions by linear regression with electronic computers. A somewhat similar discussion was given by Dyrssen and co-workers [6] in their monograph on computer calculations in analytical chemistry.

Now that electronic computers have become available, far more complex titration equations than those used in the Gran **II** method can be handled both quickly and accurately. With computers, it is also possible to fit curved lines to the points $[H]_i$, V_i. This is done in Fig. 11A, where an acid with $\log K_a = 3$ is evaluated as a strong acid. The curved line was obtained by multiple linear regression using the relation

$$[H]_i^2 = a + bV_i + c[H]_i + dV_i^2 + eV_i[H]_i \qquad (7)$$

When the coefficients a–e had been calculated, the equivalence volume was found by letting $[H] = 0$, i.e., by solving

$$dV_e^2 + bV_e + a = 0$$

which gave

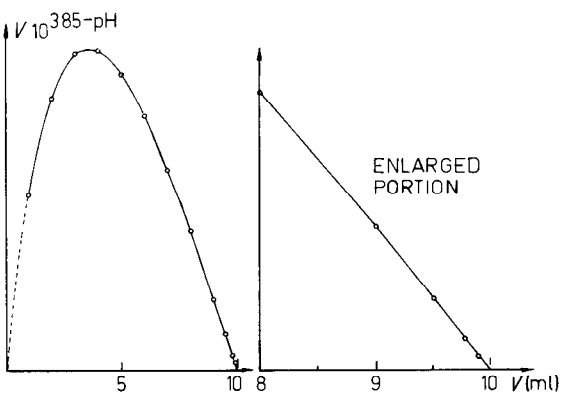

Fig. 10. Gran **II** plot of the same acid as in Fig. 9. The titration was evaluated by using the formulae for a weak acid.

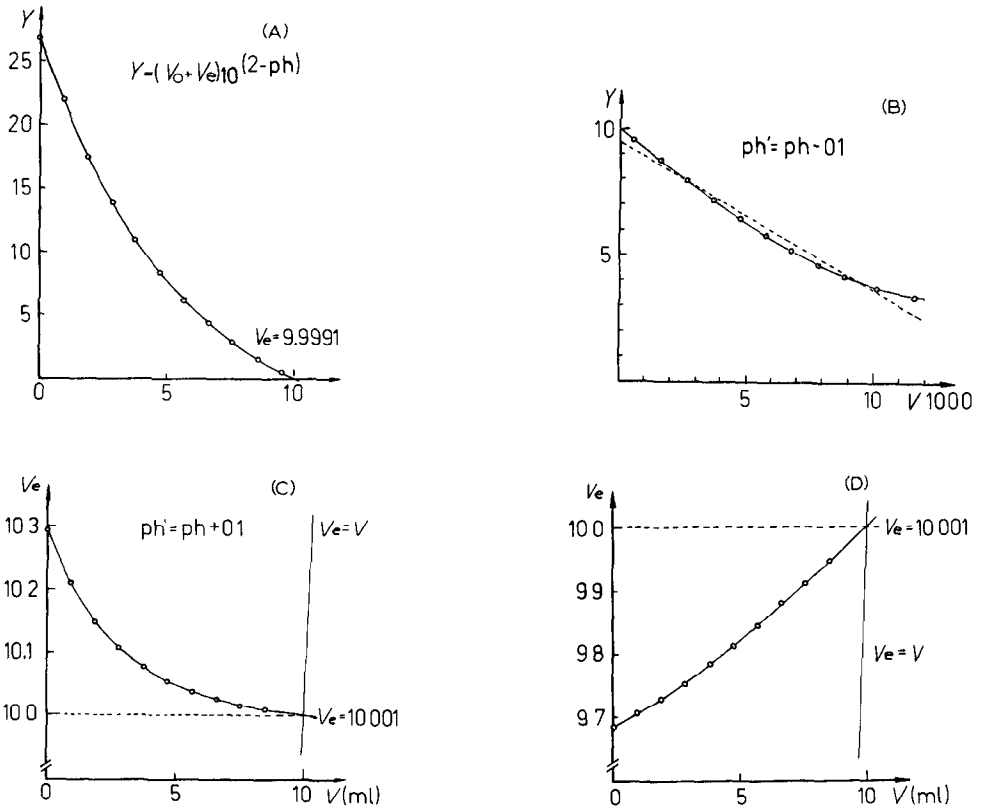

Fig. 11. The same titration as in Fig. 10 evaluated by different procedures. (A) As a strong acid by fitting a curved line to the points by linear multiple regression. (B) By the Hofstee method after changing all ph values by 0.1; the curved line was fitted to the points by linear multiple regression and gives $V_e = 10.002$ ml; the dashed line ($K = 579.4$) gives $V_e = 9.468$ ml. (C) As a weak acid by the Quoteq method. (D) As a strong acid by the Quoteq method.

$$V_e = [-b \pm (b^2 - 4\,ad)^{\frac{1}{2}}]/2d \qquad (8)$$

An easy way of making all these calculations is to use a computer with a spreadsheet program, e.g., Lotus 123, which has built-in linear regression subprogram.

THE HOFSTEE METHOD

However, in 1960 Hofstee [7] published a linear regression method of finding the equivalence volume in titrations of weak acids in which a complete titration equation was used. For the titration of a weak acid, this turns out, in principle, to be the same complete titration equation as the one derived by Ingman and Still [8] and Johansson [9].

For a weak acid, the Hofstee equation is

$$Y_i = V_e - K_a X_i \tag{9}$$

where $Y_i = V_i + [(V_0 + V_i)/C_b]\ ([H]_i - K_w/[H]_i)$

and $X_i = [H]_i\ Y_i$

In Eqn. 9, X is regarded as the independent and Y as the dependent variable, in which case Eqn. 9 is the equation for a straight line with slope $-K_a$ and V_e is the intercept of the line with the ordinate.

Pehrsson et al. [5] also investigated the Hofstee method. They stressed the advantage that the stability constant does not have to be known. However, the Hofstee method requires a very accurate calibration of the electrode system, which means that it is necessary to be able to calculate [H] with very high accuracy from measured values of E or pH. They also pointed out that the straight line should be found by regression of X on Y, i.e., Y should be regarded as the independent and X as the dependent variable, because the variable having the greater relative errors should be considered the independent variable.

If the Hofstee method is to be used in titrations of very weak acids, the electrode system should be calibrated in alkaline solutions. Further, as in the Gran methods, only points before or points after the equivalence volume should be included in the calculation, and for weak acids the point $V=0$ should normally be disregarded.

The need for accurate calibration of the electrode system is probably the most important drawback of the Hofstee method. If the calibration is bad, the points will not fall on a straight line. Both the slope and the intercept on the ordinate will then be given wrong values as will V_e and K. It is, however, not necessary to fit a straight line to the points. With a little extra work in the form of programming, a curved line of a predetermined general form can be fitted instead.

As an example, a synthetic titration of 100 ml of a 0.01 M solution of an acid with $\log K = 3$ ($K = 1000$) with 0.1 M sodium hydroxide will be discussed. When exact ph values are used, the regression comes out with $V_e = 10.000$ ml and $K = 1000.0$. If the ph values are changed so that $ph' = ph - 0.1$ and the ph' values are used in the calculations with straight line regression, then $V_e = 9.468$ ml and $K = 579.4$. However, if a branch of a suitable hyperbola is fitted to the points by linear regression, then $V_e = 10.002$ ml. A diagram with the two regression lines is shown in Fig. 11B. The hyperbola to fit is given by the equation

$$X_i Y_i = a + bY_i + cX_i + dY_i^2 \tag{10}$$

where Y is treated as the independent and X as the dependent variable. The coefficients a, b, c and d are found by linear regression by using X and Y values for various values of i. When the coefficients have been calculated, they are used in the equation

$$X=(a+bY+dY^2)/(Y-c) \tag{11}$$

Then the intersection of this curve with the line $X=0$ gives

$$dY^2+bY+a=0$$

and thus Eqn. 8 can be obtained again. A similar method was used by Gran and Johansson [10].

Even with an inaccurate calibration of the electrode system, it is thus possible to obtain a quite accurate value for the equivalence volume. It seems that there is no method available for finding an accurate value for the stability constant by using the Hofstee method if the electrode system is inaccurately calibrated.

THE EKVOL METHOD

With the general availability of electronic computers, more complete and complex equations and calculation programs can be handled in a reasonable time and with a limited amount of manpower. In 1978, Johansson and Johansson [11] published a method for the evaluation of titrations of one monoprotic acid or base. This method has a number of advantages: (a) any stability constant can be handled and it need not be known; (b) the electrode system needs only rough calibration; (c) no preliminary estimates of the equivalence volume or the stability constant are needed; and (d) the program is able to select appropriate measurements automatically.

The complete titration equation for a monoprotic acid is written

$$-K_w\frac{V_0+V}{C_b[H]}+K_a\left(V[H]+\frac{V_0+V}{C_b}[H]^2-\frac{V_0+V}{C_b}K_w\right) - V_e+\left(V+\frac{V_0+V}{C_b}[H]\right)=0 \tag{12}$$

The authors used an electrode system calibrated for hydrogen ion concentration. Readings are denoted ph to indicate that $ph=-\log[H]$. If the calibration is somewhat inaccurate, the reading is not ph but ph′ so that a systematic error Δph is obtained in every reading and $ph'=ph+\Delta ph$. Thus

$$[H']=\text{antilog}\,(-ph-\Delta ph)=[H]\ \text{antilog}\,(-\Delta ph)=f[H] \tag{13}$$

Further, $K'=fK_a$ and $K_w'=K_w/f$ and thus Eqn. 12 can be written

$$-K_w'\frac{V_0+V}{C_b[H']}+K'\left(V[H']+\frac{V_0+V}{C_b}[H']^2f-\frac{V_0+V}{C_b}K_w'\right) - V_e+\left(V+\frac{V_0+V}{C_b}[H']f\right)=0 \tag{14}$$

For a number of data pairs V_i, $[H']_i$, Eqn. 14 is solved by giving f an initial value of 1 and by giving K'_w in the second term a suitable value (e.g., log $K'_w = -13.6$). The solution yields approximate values for K'_w, K' and V_e which are further refined in various ways depending on the value obtained for K': (a) for strong acids, $\log K' \leqslant 1$; (b) for moderately strong acids, $1 < \log K' \leqslant 4$; (c) for weak acids $4 < \log K' \leqslant 9$; (d) for very weak acids $\log K' > 9$. Depending on the $\log K'$ range chosen, various terms in the complete titration equation can be neglected in order to make linear regression possible or easier.

For a strong acid, only readings below the equivalence volume (below ph' 7) are used and in that case all terms containing K' and K'_w can be neglected. In this way, the resulting equation is

$$f\{[(V_0+V)/C_b]\ [H']\} - V_e + V = 0 \tag{15}$$

which in principle is the same equation as that used for strong acids in the Gran **II** method as it can be written in the form

$$(V_0+V)\ 10^{-ph'} = (C_b/f)\ (V_e - V) \tag{15A}$$

which in turn is equivalent to Eqn. 6.

The EKVOL program can also be applied for ampholytes, diprotic acids, conditionally strong acids and a mixture of an acid and its conjugate base. A conditionally strong acid [12] is an acid added to an alkali metal salt solution of a weaker acid, where it will release an equivalent amount of the weaker acid, which can then be titrated. As the salt of the weaker acid is present in a great excess, the titration will resemble that of a strong acid.

THE QUOTEQ METHOD

In 1980–1 Gran and Johansson [10,13] introduced a method for evaluation of potentiometric titrations, which was named the QUOTEQ method. It is in principle an extension of the Gran **I** method, in which some of the drawbacks of the earlier method are eliminated.

The expressions derived can be summarized in the general equation

$$V_{e_i} = V_j + [(V_j - V_i)/(A_{ij} - 1)] \tag{16}$$

In the same manner as different terms in the complete titration equation can be neglected for various types of acids in the EKVOL program, the term A_{ij} is derived in different ways for various types of acids. In all cases, A_{ij} has the form

$$A_{ij} = f(V_i, [H']_i)/f(V_j, [H']_j) \tag{17}$$

i.e., A_{ij} is a quotient between two similar expressions containing V and $[H]$. This quotient is the reason for the name chosen for the method. When the method is used, j is the number of a data point, usually before and close to the equivalence volume, and i is given values $< j$. As examples, the following

expressions can be given for strong acids and weak acids with $4<\log K<7$, respectively:

$$A_{ij}=(V_0+V_i)[\mathrm{H}']_i/(V_0+V_j)[\mathrm{H}']_j \tag{18}$$

$$A_{ij}=\{C_b V_i[\mathrm{H}']_i+(V_0+V_i)[\mathrm{H}']_i^2\}/\{C_b V_j[\mathrm{H}']_j+(V_0+V_j)[\mathrm{H}']_j^2\} \tag{19}$$

The QUOTEQ method was developed for all kinds of monoprotic acids and of course equivalent equations can be derived and used for the titration of various bases with strong acids.

In titrations with an accurately calibrated electrode system, the same V_e value should be obtained for all data pairs V_i, $[\mathrm{H}]_i$ where $[\mathrm{H}]_i$ is calculated from $[\mathrm{H}]=\mathrm{antilog}(-\mathrm{ph})$ and $\mathrm{ph}=(E_0-E)/Q$, the calibration being made for hydrogen ion concentration. Thus if the V_e values obtained for various data points V_i, $[\mathrm{H}]_i$ were plotted versus V_i, a number of points lying on a horizontal straight line would be obtained.

If the calibration is somewhat inaccurate or the titration equation used is too approximate, the points will usually fall on a curved line. Experience has shown that, by fitting a suitable curved line by regression and extrapolating the curved line until it intersects the line $V_e=V$, as shown in Fig. 11C, a quite accurate value for V_e can be obtained. In this case, values for a synthetic titration were used and all ph values were displaced by 0.1 units. The expression used was Eqn. 19. In fact, Eqn. 19 in combination with the curved regression line of V_e on V_i can be used for all acids with $2<\log K_a<7$. In this case, the hyperbola to fit is given by

$$V_{ei}V_i=a+bV_i+cV_{ei}+dV_i^2 \tag{20}$$

The coefficients a, b, c and d are found by linear regression from the V_e and V values for various values of i. When the coefficients have been calculated, they are used in the equation

$$V_e=(a+bV+dV^2)/(V-c) \tag{21}$$

Then the intersection of this curve with the line $V_e=V$ gives

$$V_e=\{-(b+c)\pm[(b+c)^2-4a(d-1)]^{1/2}\}/2(d-1) \tag{22}$$

As this regression fits the curve very closely to the points, the choice of the expression A_{ij} is not very critical. This is shown in Fig. 11D, where the same titration as in Fig. 11C was evaluated as a strong acid. In this case, it does of course not matter whether the ph values were displaced or not, because in principle only the expression $(\mathrm{ph}_i-\mathrm{ph}_j)$ is used in the calculation.

The QUOTEQ method was developed to handle monoprotic acids with $\log K<10$, di- and tri-protic acids for which the last jump in the titration curve is reasonably large, and conditionally strong acids. It was shown that the method could be used in the standardization of a sodium hydroxide solution against a

known hydrochloric acid solution, for example, even without knowledge of E_0 and the junction potential coefficient j_{H^+}. It is also possible to use it for the determination of E_0 and j_{H^+}. In a later paper [14], the QUOTEQ method was applied successfully to precipitation titrations of chloride with silver and fluoride with lanthanum, in which due regard was given to a number of possible side-reactions.

NONLINEAR REGRESSION METHODS

In all the methods discussed so far, there is normally no need to start the calculations by feeding approximate values for the different variables into the equations used. In some procedures, iteration is used, e.g., in calculation of stability constants. In such cases, the number of loops can be greatly reduced if appropriate values can be entered before the calculation starts.

The methods discussed above can be characterized as linear regression methods. They have a number of advantages; for example, they can be used with calculators of rather limited capacity, even programmable pocket calculators.

In 1973, Ingman et al. [15] described a nonlinear program called TITRA for the evaluation of titrations of quite complex mixtures of acids, polyprotic acids, acids in mixtures with weak bases and ampholytes. The program was later further improved by Pehrsson et al. [5, 16]. Nonlinear methods are usually more powerful than the linear ones, but in many cases they require quite good initial estimates in order to converge versus proper values for the variables to be calculated. The nonlinear methods and programs are, however, another story.

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