Determination of the Equivalence Point in Potentiometric Titrations. Part II*

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Summary

When the potential - volume curve obtained during potentiometric titrations shows only a small potential change at the end-point, it has been customary to plot a $\Delta E/\Delta V$ - volume curve and to take the peak of this curve as the equivalence point. In 1950 the author proposed a method of transforming these curves by a numerical manipulation into straight lines intersecting at the equivalence point. In this paper another way of transforming titration curves into straight lines has now been developed.

A simple theoretical treatment shows that the method can be applied to titrations involving acids and bases, ionic precipitations, formation of complexes, and oxidation - reduction reactions. To facilitate the use of the method a table has been compiled giving quantities to be calculated and plotted against volume of titrant added. These quantities can be evaluated by simple slide rule calculations and, since straight line relationships hold, end-points can be obtained by simple extrapolation.

The practice of the method is applicable to potentiometers calibrated either in millivolts or in pH units, even when titrations other than acid - alkali reactions are in use.

Résumé

Quand la courbe potentiel - volume obtenue au cours des titrages potentiométriques ne montre qu'un petit changement de potentiel au point d'équivalence on a l'habitude de tracer la courbe $\Delta E/\Delta V$-volume et d'appeler le sommet de cette courbe le point d'équivalence. En 1950 l'auteur avait proposé une méthode pour transformer, par une façon de calcul, ces courbes en lignes droites s'entrecoupant au point d'équivalence. Dans ce rapport une autre maniere a été développee pour transformer ces courbes de titration en lignes droites.

Un traitement théorique simple démontre que cette méthode peut etre appliquée au titrage d'acides et bases, aux précipitations ioniques, à la formation de complexes et à l'oxydimétrie. On a compilé un tableau, afin de faciliter l'emploi de la méthode, donnant les quantités à calculer et à tracer contre le volume de solution titrante. Ces quantités peuvent être calculées simplement à l'aide d'une règle à calcul, et on peut obtenir les points d'équivalence simplement par l'extrapolation, puisqu'il existe une proportionnalité directe.

On peut se servir d'un potentiomètre gradué en unités de pH aussi bien qu'en millivolts, même quand les titrages envisagés ne sont pas limités à la neutralisation d'acides et bases.

Zusammenfassung

Wenn die bei der potentiometrischen Titration erhaltene Potential - Volumenkurve nur eine geringe Potentialänderung beim Neutralpunkt aufweist, so war es üblich eine $\Delta E/\Delta V$ - Volumenkurve aufzutragen und den Scheitel dieser Kurve als Äquivalenzpunkte anzusprechen. Im Jahre 1950 hatte der Verfasser eine Methode vorgeschlagen, diese Kurven rechnerisch in Gerade umzuwandeln, die sich im Äquivalenzpunkt schneiden. Im

* For details of part I of this series (not in *The Analyst*) see reference list, p. 670.

vorliegenden Bericht wird ein anderer Weg eingeschlagen, um diese Titrationskurven in gerade Linien umzuwandeln.

Einfache theoretische Überlegungen zeigen, dass diese Methode für Titrationen angewendet werden kann, die Säuren und Basen, Ionen-Niederschläge, Komplexbildung und Oxydations-Reduktions-Reaktionen umfassen. Um den Gebrauch dieser Methode zu erleichtern, wurde eine Tabelle ausgearbeitet, bei der die zu berechnende Grösse gegen das Titrationsvolumen aufgetragen wird. Diese Grössen werden mit Hilfe eines Rechenschiebers ermittelt und die Neutralpunkte werden, da lineare Beziehungen bestehen, durch Extrapolation ermittelt.

Diese Methode kann für Potentiometer angewendet werden, die für Millivolt oder pH-Einheiten geeicht sind, auch wenn nicht acidimetrische Titrationen ausgeführt werden.

THE equivalence point in a potentiometric titration is generally determined by finding, in some way or other, the point of maximum slope of the titration curve. In many instances there are very sharp breaks in these curves and there is no difficulty in finding the equivalence point. At other times, however, such as when very weak acids are titrated with strong bases, the curves are more difficult to evaluate. It is then usual to plot the differential curves, $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ against volume of titrant added. The peak on these curves corresponds to the point of maximum slope of the normal titration curve. Results obtained by this method or other similar methods based on the determination of the point of maximum slope may be in error if the titration curve is not symmetrical about the equivalence point, *e.g.*, in titrations of silver ions with chromate ions.

About two years ago the author proposed a method[1] that overcame these difficulties. This method was based on the fact that the differential curves $\Delta V/\Delta pH$ or $\Delta V/\Delta E$ have two branches intersecting at the equivalence point. For weak electrolyte systems the branches will be more or less parabolic in shape, but by appropriate mathematical manipulations they can be transformed into straight lines. This is a great advantage when the curves must be extrapolated.

Recently Sørensen[2,3] pointed out that graphs very similar to those obtained by the present author were obtained if the antilogarithm of the pH was plotted as a function of the volume of titrant added. Sørensen, however, did not study reactions other than the neutralisation titrations of strong and weak acids with strong bases and the precipitation titration of chloride ions with silver ions. The scope of this paper is to investigate more fully the possibilities of Sørensen's method, especially for more complicated titrations such as ion-combination titrations, including ions of different valencies, and to show that it has advantages over other methods.

THEORY

The theoretical background for the new method is outlined in the following section.

NEUTRALISATION TITRATIONS

STRONG ACID - STRONG BASE—

If V_o ml of a strong acid, with original concentration in gram-equivalents per litre of C_A, is titrated with a strong base of concentration C_B, the concentration of hydrogen ions, after the addition of V ml of base, will be—

$$C_{H\cdot} = C_A \frac{V_o}{V_o + V} - C_B \frac{V}{V_o + V}. \quad .. \quad .. \quad .. \quad (1)$$

At the equivalence point—

$$C_A V_o = C_B V_e, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where V_e is the volume of base added when the equivalence point is reached.

Substituting in equation (1) we get—

$$C_{H\cdot} = C_B \frac{V_e - V}{V_o + V}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

Now since antilog $x = 10^x$—

$$\text{antilog } (-pH) = 10^{-pH} = a_{H\cdot} = f_{H\cdot} \times C_{H\cdot}. \quad .. \quad .. \quad (4)$$

Equations (3) and (4) together give—

$$10^{-pH} = f_{H^+} \times \frac{C_B}{V_o + V}(V_e - V), \quad .. \quad .. \quad .. \quad (5)$$

which can be transformed to—

$$(V_o + V)10^{-pH} = f_{H^+} \times C_B(V_e - V), \quad .. \quad .. \quad .. \quad (6)$$

or more generally to—

$$(V_o + V)10^{k_1 - pH} = k_2(V_e - V), \quad .. \quad .. \quad .. \quad (7)$$

where k_1 and k_2 are constants including the activity factor, which, in most instances, can be considered constant during a titration.

When the equivalence point has been passed—

$$C_{OH'} = C_B \frac{V}{V_o + V} - C_A \frac{V_o}{V_o + V} \quad .. \quad .. \quad .. \quad (8)$$

$$= \frac{C_B}{V_o + V}(V - V_e) \quad .. \quad .. \quad .. \quad .. \quad (8a)$$

and further—

$$C_{H^+} = \frac{k_w}{C_{OH'}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

which together with equation (4) gives—

$$\text{antilog pH} = 10^{pH} = \frac{C_B}{f_{H^+} \times k_w(V_o + V)}(V - V_e) \quad .. \quad .. \quad (10)$$

or, more generally—

$$(V_o + V)10^{pH - k_3} = k_4(V - V_e). \quad .. \quad .. \quad .. \quad (11)$$

Sørensen did not make any correction for the increase in volume of the solution during the titration and did not obtain linear graphs. This correction is, however, easily made in the same way as in conductimetric titrations, as can be seen in equations (7) and (11) above.

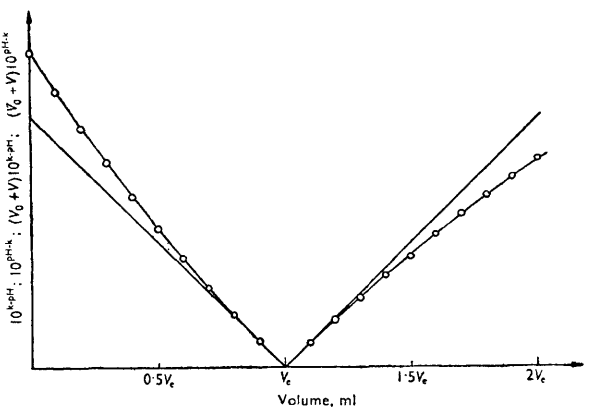

Fig. 1. Titration of 40 ml of 0·025 *N* hydrochloric acid with 0·1 *N* sodium hydroxide
—o—o— Curves according to Sørensen
———— Curves according to proposed method

An example of a titration of a strong acid with a strong base is shown in Fig. 1, and it is evident that the straight lines obtained by applying the correction for the volume increase make the determination of the equivalence point much more reliable.

WEAK ACID - STRONG BASE—

The formulae derived below apply to moderately weak acids such as acetic acid.

V_o ml of a weak acid, HA, with original concentration C_A, is titrated with a strong base of concentration C_B. For weak acids—

$$a_{H^+} = k_a \frac{C_{HA}}{C_{A'}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

where—

$$C_{HA} = C_A \frac{V_o}{V_o + V} - C_B \frac{V}{V_o + V} = \frac{C_B}{V_o + V}(V_e - V) \quad .. \quad .. \quad (13)$$

and

$$C_{A'} = \frac{C_B}{V_o + V} V. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

These three equations together give—

$$a_{H^+} = k_a \frac{V_e - V}{V}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (15)$$

which, together with equation (4), leads to—

$$\text{antilog } (-\text{pH}) = 10^{-\text{pH}} = \frac{k_a}{V}(V_e - V) \quad .. \quad .. \quad (16)$$

The last equation can be transformed into a more general form analogous to equations (7) and (11)—

$$V \times 10^{k_b - \text{pH}} = k_b (V_e - V). \quad .. \quad .. \quad .. \quad .. \quad (17)$$

After the equivalence point has been reached equations (10) or (11) should be used.

For a dibasic acid, H_2A, the following equation will be valid after the first equivalence point has been passed—

$$a_{H^+} = k_a'' \frac{C_{HA'}}{C_{A''}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

where

$$C_{HA'} = C_A \frac{2V_o}{V_o + V} - C_B \frac{V}{V_o + V} = \frac{C_B}{V_o + V}(V_{e_2} - V), \quad .. \quad (19)$$

where V_{e_2} indicates the second equivalence point, and—

$$C_{A''} = \frac{C_B}{V_o + V}(V - V_{e_1}) \quad .. \quad .. \quad .. \quad .. \quad (20)$$

These last three equations give—

$$a_{H^+} = k_a'' \frac{V_{e_2} - V}{V - V_{e_1}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (21)$$

which, together with equation (4), gives—

$$\text{antilog } (-\text{pH}) = 10^{-\text{pH}} = k_a'' \frac{V_{e_2} - V}{V - V_e}. \quad .. \quad .. \quad .. \quad (22)$$

In determining the first equivalence point this equation should be used in the form—

$$(V_{e_2} - V)10^{\text{pH} - k_7} = k_8 (V - V_{e_1}) \quad .. \quad .. \quad .. \quad .. \quad (23)$$

and for the second equivalence point equation (22) is rewritten to give—

$$(V - V_{e_1})10^{k_9 - \text{pH}} = k_{10} (V_{e_2} - V). \quad .. \quad .. \quad .. \quad .. \quad (24)$$

The use of equation (23) presupposes knowledge of the second equivalence point, V_{e_2}, but as for this purpose V_{e_2} need not necessarily be known exactly, it may be estimated with sufficient accuracy directly from the titration curve.

The use of equation (24) in the same way requires knowledge of the first equivalence point, V_{e_1}, which, however, is usually determined before the second equivalence point.

After the second equivalence point has been passed, equations (10) and (11) should be used, as with monobasic acids.

As seen from equations (17), (23) and (24), the correction factors influence the results much more for weak acids than for strong acids. This is illustrated in Fig. 2, where the curves obtained by the Sørensen method and by the proposed method are shown. It is evident that the former curves are noticeably non-linear, while the latter pair are linear.

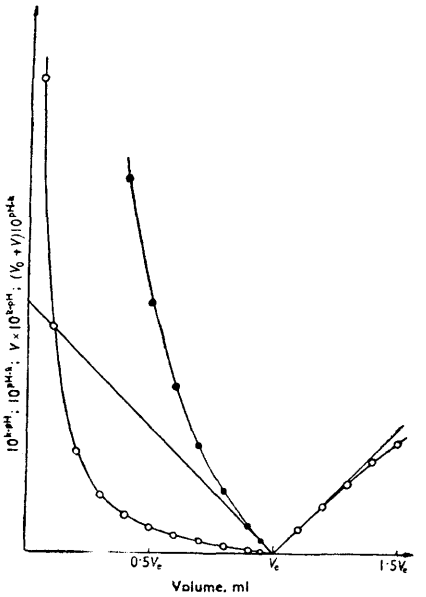

Fig. 2. Titration of 40 ml of 0·025 *N* weak acid (HA) with 0·1 *N* sodium hydroxide
—o—o— Curves according to Sørensen
—●—●— Enlarged section of curve according to Sørensen
———— Curves according to proposed method

For polymeric weak acids, *e.g.*, polymethacrylic acid, Katchalsky and Spitnik[4] have shown that the titration curve follows the generalised Henderson - Hasselbach equation—

$$\mathrm{pH} = \mathrm{pk_a} - n \log \frac{1-\alpha}{\alpha}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (25)$$

or

$$a_{\mathrm{H}^+} = \mathrm{k_a}\left(\frac{C_{\mathrm{HA}}}{C_{\mathrm{A}^-}}\right)^n. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (25a)$$

With the same nomenclature as before, the following equations are obtained:

$$a_{\mathrm{H}^+} = \mathrm{k_a}\left(\frac{V_e - V}{V}\right)^n \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (26)$$

and

$$\text{antilog } (-\mathrm{pH}) = 10^{-\mathrm{pH}} = \mathrm{k_a}\left(\frac{V_e - V}{V}\right)^n, \quad .. \quad .. \quad .. \quad (27)$$

which can be transformed to—

$$V \times 10^{\frac{\mathrm{k_{11}} - \mathrm{pH}}{n}} = \mathrm{k_{12}}\,(V_e - V). \quad .. \quad .. \quad .. \quad .. \quad .. \quad (28)$$

Ion-combination titrations

Precipitation titrations—

When V_o ml of a solution of a substance (A), with original concentration C_{A_o}, is titrated

with a solution of a substance (B), of concentration C_{B_o}, a precipitate (A_xB_y) is formed according to the reaction—

$$xA + yB = A_xB_y \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (29)$$

As long as A is present in excess:

$$C_A = C_{A_o} \frac{V_o}{V_o + V} - \frac{x}{y} C_{B_o} \frac{V}{V_o + V} \quad .. \quad .. \quad .. \quad .. \quad (30)$$

$$= \frac{x}{y} \times \frac{C_{B_o}}{V_o + V} (V_e - V). \quad .. \quad .. \quad .. \quad .. \quad .. \quad (30a)$$

If the potential is given by—

$$E = E^\circ_A + \frac{RT}{n_A.F} \log_e C_A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (31)$$

$$= E^\circ_A + 2{\cdot}30 \frac{RT}{n_A.F} \log C_A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (31a)$$

E°_A a constant, can be written

$$E^\circ_A = 2{\cdot}30 \frac{RT}{n_AF} \log K^\circ_A, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (32)$$

which, together with equation (31*a*), will give—

$$E = 2{\cdot}30 \frac{RT}{n_AF} \log (K^\circ_A C_A) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (33)$$

or

$$\log (K^\circ_A C_A) = \frac{E}{2{\cdot}30 \frac{RT}{n_AF}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (33a)$$

which at room temperature assumes the forms—

$$\log (K^\circ_A C_A) = 17\, n_A E \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (33b)$$

or

$$C_A = \frac{1}{K^\circ_A} \times 10^{17\, n_A E}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (33c)$$

Equations (30*a*) and (33*c*) together give—

$$\frac{1}{K^\circ_A} \times 10^{17\, n_A E} = \frac{x}{y} \times \frac{C_{B_o}}{V_o + V} (V_e - V), \quad .. \quad .. \quad .. \quad (34)$$

which can be written more generally as—

$$(V_o + V)\ 10^{17\, n_A (E - k_{13})} = k_{14}(V_e - V). \quad .. \quad .. \quad .. \quad (35)$$

When B is present in excess—

$$C_B = C_{B_o} \frac{V}{V_o + V} - \frac{y}{x} \times C_{A_o} \frac{V}{V_o + V} \quad .. \quad .. \quad .. \quad (36)$$

$$= \frac{C_{B_o}}{V_o + V} (V - V_e). \quad .. \quad .. \quad .. \quad .. \quad .. \quad (36a)$$

The concentration of A is then related to the concentration of B by the equation—

$$C^x_A\ C^y_B = S, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (37)$$

where S is the solubility product of the precipitate A_xB_y. Equations (33*c*), (36*a*) and (37) give—

$$\frac{1}{K^\circ_A} \times 10^{17\, n_A E} = \frac{\frac{1}{S^x}}{\left[\frac{C_{B_o}}{V_o + V} (V - V_e)\right]^{\frac{x}{y}}}, \quad .. \quad .. \quad .. \quad (38)$$

which can be transformed to:

$$(V_o + V) \times 10^{\frac{x}{y} \times 17 n_A (k_{15} - E)} = k_{16} (V - V_e) \quad .. \quad .. \quad .. \quad (39)$$

When $x = y = n_A = 1$, equations (35) and (39) are analogous to equations (7) and (11), respectively.

If the potential is controlled, not by the concentration of A, but by the concentration of B, it can be shown that the equations—

$$(V_o + V) \times 10^{\frac{y}{x} \times 17 n_B (k_{17} - E)} = k_{18} (V_e - V) \quad .. \quad .. \quad .. \quad (40)$$

and

$$(V_o + V) \times 10^{17 n_B (E - k_{19})} = k_{20} (V - V_e) \quad .. \quad .. \quad .. \quad (41)$$

hold before and after the equivalence point, respectively.

COMPLEX-FORMATION TITRATIONS—

When V_o ml of a solution of a substance A, with original concentration C_{A_o}, is titrated with a solution of a substance B, of concentration C_{B_o} a complex is formed according to the reaction—

$$xA + yB = A_x B_y. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (42)$$

The extent to which this reaction proceeds is given by the relationship—

$$\frac{C_A^x \, C_B^y}{C_{A_x B_y}} = K_C, \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (43)$$

where K_C is the complex constant. As long as A is present in excess,

$$C_A = \frac{x}{y} \times \frac{C_{B_o}}{V_o + V} (V_o + V) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (30a)$$

This equation leads to the resul s (34) and (35) in the preceding section.

When B is present in excess—

$$C_B = \frac{C_{B_o}}{V_o + V} (V - V_e) \; .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (36a)$$

and

$$C_{A_x B_y} = \frac{1}{y} \times \frac{C_{B_o}}{V_o + V} V_e. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (44)$$

Equations (36*a*), (43) and (44) together give—

$$C_A = K_C^{\frac{1}{x}} \frac{\left[\dfrac{C_{B_o} V_e}{y(V_o + V)}\right]^{\frac{1}{x}}}{\left[\dfrac{C_{B_o}(V - V_e)}{V_o + V}\right]^{\frac{y}{x}}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (45)$$

which, together with (33*c*), gives—

$$\frac{1}{K_A^o} \times 10^{17 n_A E} = K_C^{\frac{1}{x}} \frac{\left[\dfrac{C_{B_o} \cdot V_e}{y(V_o + V)}\right]^{\frac{1}{x}}}{\left[\dfrac{C_{B_o}(V - V_e)}{V_o + V}\right]^{\frac{y}{x}}} \quad .. \quad .. \quad .. \quad .. \quad (46$$

which is transformed to the more general form—

$$(V_o + V)^{1 - \frac{1}{y}} \times 10^{\frac{x}{y} \times 17 n_A (k_{21} - E)} = k_{22} (V_e - V). \quad .. \quad .. \quad (47)$$

If $y = 1$, equation (47) takes the form—

$$10^{x \times 17 n_A (k_{23} - E)} = k_{24} (V_e - V). \quad .. \quad .. \quad .. \quad .. \quad (47a)$$

If the potential is controlled by the concentration of the substance B, the equations—

$$(V_o + V)^{1-\frac{1}{x}} V^{\frac{1}{x}} \times 10^{\frac{y}{x} \times 17 n_B (k_{25} - E)} = k_{26}(V - V_e) \quad .. \quad .. \quad (48)$$

or, if $x = 1$—

$$V \times 10^{y \times 17 n_B (k_{27} - E)} = k_{28}(V - V_e) \quad .. \quad .. \quad .. \quad .. \quad (48a)$$

hold before, and equation (41) after, the equivalence point is reached.

Oxidation - reduction titrations

When V_o ml of a solution of a substance A in its reduced state, with original concentration C_A, is titrated with a solution of a substance B in its oxidised state, of concentration C_B, the following reactions take place in the solution—

$$A_{red} = A_{ox} + n_A e^- \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (49)$$

and

$$B_{ox} + n_B e^- = B_{red}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (50)$$

Up to the equivalence point—

$$C_{A_{ox}} = \frac{n_B}{n_A} \times \frac{C_B}{V_o + V} V \quad .. \quad .. \quad .. \quad .. \quad .. \quad (51)$$

and

$$C_{A_{red}} = C_A \frac{V_o}{V_o + V} - \frac{n_B}{n_A} \times \frac{C_B}{V_o + V} V \quad .. \quad .. \quad .. \quad (52)$$

$$= \frac{n_B}{n_A} \times \frac{C_B}{V_o + V} V \quad .. \quad .. \quad .. \quad .. \quad .. \quad (52a)$$

The potential is given by—

$$E = E^\circ_A + \frac{RT}{n_A F} \times \log_e \frac{C_{A_{ox}}}{C_{A_{red}}}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (53)$$

which, by analogy with equation (31), can be rewritten to give—

$$\frac{C_{A_{ox}}}{C_{A_{red}}} = \frac{1}{K^\circ_A} \times 10^{17 n_A E}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (54)$$

Equations (51), (52) and (54) together give—

$$\frac{V}{V_o + V} = \frac{1}{K^\circ_A} \times 10^{17 n_A E}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (55)$$

which can be transformed to the more general form—

$$V \times 10^{17 n_A (k_{29} - E)} = k_{30}(V_e - V) \quad .. \quad .. \quad .. \quad .. \quad (56)$$

When the equivalence point has been passed—

$$C_{B_{red}} = \frac{n_A}{n_B} \times C_A \frac{V_e}{V_o + V} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (57)$$

$$= \frac{C_B}{V_o + V} V_e \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (57a)$$

and

$$C_{B_{ox}} = C_B \frac{V}{V_o + V} - \frac{n_A}{n_B} \times C_A \frac{V_o}{V_o + V} \quad .. \quad .. \quad .. \quad (58)$$

$$= \frac{C_B}{V_o + V}(V - V_e). \quad .. \quad .. \quad .. \quad .. \quad .. \quad (58a)$$

By analogy with equation (54)—

$$\frac{C_{B_{ox}}}{C_{B_{red}}} = \frac{1}{K^\circ_B} \times 10^{17 n_B E}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (59)$$

Equations (57*a*), (58*a*) and (59) give—

$$\frac{V - V_e}{V_e} = \frac{1}{K^o_B} \times 10^{17n_B E}, \quad \ldots \quad (60)$$

which can be transformed to the form—

$$10^{17n_B(E - k_{31})} = k_{32}(V - V_e). \quad \ldots \quad (61)$$

Conclusions

In order to facilitate the use of this method, the appendix (below) has been compiled. In each type and stage of titration the expression to be plotted against the consumption of titrant, V, is given. The expressions are given both in a simple form leading to slightly curved lines and in a corrected form leading to straight lines which facilitate extrapolation. In all the expressions, the constant "k" is arbitrary and should be given a value such that the antilogarithms will fall in a suitable range such as 0 to 100–1000. It is generally most convenient to give "k" values in whole pH-units or in hundreds of millivolts.

Many potentiometers used in analytical laboratories are equipped with a double scale indicating millivolts or pH units. In this case the calculations are facilitated if the readings are taken from the pH scale even in titrations other than neutralisation titrations. The expressions to be plotted are then simplified by substituting the "pH" value for the product "17E," *e.g.*—

$$10^{n_A(\text{"pH"} - k)}$$

should be calculated instead of—

$$10^{17n_A(E - k)}.$$

Discussion

Many rather complicated expressions have been put forward in the preceding theoretical section and it may be thought that considerable work would be involved in using the proposed method for finding the equivalence point. In most instances, however, all the calculations required can be made with the help of a slide rule. Further, if the dilution during the titration is negligible, the correction for the dilution can usually be dispensed with. For weak electrolyte systems—titrations of weak acids and bases, complex formation and redox titrations—the correction factor should preferably be included. Most trouble is experienced in complex-formation titrations in systems of the type—

$$xA + yB = A_xB_y,$$

where $x \neq y \neq 1$, and in such systems, the method developed previously[1] is often simpler. The great advantage of both these methods is that they lead to linear graphs, which can be extrapolated if necessary.

APPENDIX

Expressions to be calculated and plotted against volume V of titrant added

Titration	Simple form	Corrected form giving straight lines
A. Strong acid - strong base—		
1. Before end-point ..	10^{k-pH}	$(V_o + V) \times 10^{k-pH}$
2. After end-point ..	10^{pH-k}	$(V_o + V) \times 10^{pH-k}$
B. Weak acid - strong base—		
(*a*) *Monobasic acid*—		
1. Before end-point ..	A.1	$V \times 10^{k-pH}$
2. After end-point ..	A.2	A.2
(*b*) *Dibasic acid*—		
1. Before 1st end-point	A.1	B(*a*)1
2. After 1st end-point ..	A.2	$(V_{e_2} - V) \times 10^{pH-k}$
3. Before 2nd end-point	A.1	$(V - V_{e_1}) \times 10^{k-pH}$
4. After 2nd end-point	A.2	A.2

(*c*) *Polymeric acid*—

1. Before end-point	..	$10^{\frac{k-pH}{n}}$	$V \times 10^{\frac{k-pH}{n}}$
2. After end-point	..	A.2	A.2

C. PRECIPITATION TITRATIONS: $xA + yB = A_xB_y$—

(*a*) *Potential controlled by* C_A—

1. Before end-point	..	$\begin{cases} 10^{17n_A(E-k)} \\ 10^{n_A(\text{"pH"}-k)} \end{cases}$	$\begin{cases} (V_o+V)\times 10^{17n_A(E-k)} \\ (V_o+V)\times 10^{n_A(\text{"pH"}-k)} \end{cases}$
2. After end-point	..	$\begin{cases} 10_y^{x\times 17n_A(k-E)} \\ 10_y^{x\times n_A(k-\text{"pH"}} \end{cases}$	$\begin{cases} (V_o+V)\times 10_y^{x\times 17n_A(k-E)} \\ (V_o+V)\times 10_y^{x\times n_A(k-\text{"pH"})} \end{cases}$

(*b*) *Potential controlled by* C_B—

1. Before end-point	..	$\begin{cases} 10^{\frac{y}{x}\times 17n_B(k-E)} \\ 10^{\frac{y}{x}\times n_B(k-\text{"pH"})} \end{cases}$	$\begin{cases} (V_o+V)\times 10^{\frac{y}{x}\times 17n_B(k-E)} \\ (V_o+V)\times 10^{\frac{y}{x}\times n_B(k-\text{"pH"}} \end{cases}$
2. After end-point	..	$\begin{cases} 10^{17n_B(E-k)} \\ 10^{n_B(\text{"pH"}-k)} \end{cases}$	$\begin{cases} (V_o+V)\times 10^{17n_B(E-k)} \\ (V_o+V)\times 10^{n_B(\text{"pH"}-k)} \end{cases}$

D. COMPLEX-FORMATION TITRATIONS: $xA + yB = A_xB_y$—

(*a*) *Potential controlled by* C_A—

1. Before end-point	..	C(*a*)1	C(*a*)1
2. After end-point	..	C(*a*)2	$\begin{cases} (V_o+V)^{1-\frac{1}{y}}\times 10^{\frac{x}{y}\times 17n_A(k-E)} \\ (V_o+V)^{1-\frac{1}{y}}\times 10^{\frac{x}{y}\times n_A(k-\text{"pH"})} \end{cases}$

(*b*) *Potential controlled by* C_B—

1. Before end-point	..	C(*b*)1	$\begin{cases} (V_o+V)^{1-\frac{1}{x}}\times V^{\frac{1}{x}}\times 10^{\frac{x}{y}\times n_A(k-E)} \\ (V_o+V)^{1-\frac{1}{x}}\times V^{\frac{1}{x}}\times 10^{\frac{y}{x}\times n_A(k-\text{"pH"})} \end{cases}$
2. After end-point	..	C(*b*)2	C(*b*)2

E. OXIDATION - REDUCTION TITRATIONS—

(*a*) $n_BA_{red} + n_AB_{red} = n_BA_{ox} + n_AB_{ox}$—

1. Before end-point	..	$\begin{cases} 10^{17n_A(k-E)} \\ 10^{n_A(k-\text{"pH"})} \end{cases}$	$\begin{cases} V\times 10^{17n_A(k-E)} \\ V\times 10^{n_A(k-\text{"pH"})} \end{cases}$
2. After end-point	..	$\begin{cases} 10^{17n_B(E-k)} \\ 10^{n_B(\text{"pH"}-k)} \end{cases}$	$\begin{cases} 10^{17n_B(E-k)} \\ 10^{n_B(\text{"pH"}-k)} \end{cases}$

(*b*) $n_BA_{ox} + n_AB_{red} = n_BA_{red} + n_AB_{ox}$—

1. Before end-point	..	$\begin{cases} 10^{17n_A(E-k)} \\ 10^{n_A(\text{"pH"}-k)} \end{cases}$	$\begin{cases} V\times 10^{17n_A(E-k)} \\ V\times 10^{n_A(\text{"pH"}-k)} \end{cases}$
2. After end-point	..	$\begin{cases} 10^{17n_B(k-E)} \\ 10^{n_B(k-\text{"pH"}} \end{cases}$	$\begin{cases} 10^{17n_B(k-E)} \\ 10^{n_B(k-\text{"pH"}} \end{cases}$

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NOTE.—Reference 1 is to part I of this series.

DEPARTMENT OF ANALYTICAL CHEMISTRY
SWEDISH FOREST PRODUCTS RESEARCH LABORATORY
STOCKHOLM Ö, SWEDEN

April 21st, 1952

Discussion

Dr. A. J. Lindsey (Rickmansworth) (*Chairman*) asked how long a titration of this type would take and if the calculations were readily made.

Mr. Gran gave as an example the results for a titration of 100 ml of a solution that contained 1 milli-equivalent of a strong acid with a 0·1 *N* solution of a strong base. The V_e would theoretically be 10 ml. Readings at every millilitre would give values as follows—

V, ml	pH	$10^{(4-pH)}$	$10^{(4-pH)} \times \frac{100 + V}{100}$
0	2·00	100	100
1	2·05	89	90
2	2·105	78·5	80
3	2·17	68	70
4	2·24	57·5	60
5	2·32	47·5	50
6	2·425	37·5	40
7	2·55	28	30
8	2·73	18·5	20
9	3·04	9·2	10
10	7·00	0·001	0

The calculations were extremely simple and could be done during the titration. If the curve was also plotted at the same time, the results would be at hand 1 minute or so after the last reading had been taken.

Professor L. G. Sillén (Stockholm) said that he had seen the author's first method in action. Some ten or fifteen workers had used it successfully in Stockholm. It appeared to be easy and to cause no trouble. The second method should not be more difficult or time-consuming, and chemists might save time and gain accuracy by studying these methods and giving them a fair trial.

Mr. E. Bishop (Newcastle-on-Tyne) confirmed the author's remarks about the difficulty of accurately using the dE/dV method without precise measurement of potential to ± 10 microvolts and its attendant difficulties, and expressed interest in the possibility of the new methods. He asked whether the author's method did in fact locate the equivalence point and not the end-point, and where these were different, whether there was any indication of the difference. He enquired whether precise experimental data on redox reactions for discovering how nearly the end-point by this method coincided with the end (or equivalence) point calculated from the true weight of pure material, was available.

Mr. Gran replied that neither of his methods could locate the theoretical equivalence point, as all methods were more or less uncertain owing to human limitations, but he thought his methods gave end-points that approached the theoretical equivalence point much more closely than did that obtained by the old peak curve, especially where the titration curve was asymmetrical about the equivalence point.

Many experiments on redox reactions did not coincide with theory because of the irreversibility of redox reactions—at least, of those involving hydrogen ions. The slope of the curves obtained by the first method often was quite unexpected. The end-point, however, was mostly close to the theoretical value of the equivalence point.

Dr. A. Johansson (Stockholm) said that he thought the calculations could be simplified considerably if antilogarithmic - linear paper was used. Then it was only necessary to plot pH values that had been read from the potentiometer against volume of reagent.

Mr. Gran said that antilogarithmic paper would most certainly be of great help, as most calculations could then be dispensed with. However, such paper was not available in Sweden.