

## Determination of the Equivalent Point in Potentiometric Titrations

GUNNAR GRAN

*Department of Analytical Chemistry, Swedish Forest Products Research Laboratory,  
Stockholm, Sweden*

The equivalent point in potentiometric titrations is generally determined by plotting  $E$  or pH as a function of volume ( $V$ ) of reagent added<sup>1a</sup>. The equivalent point is said to lie at the inflexion point of the curve, *i. e.*, at the point of maximum slope. This, however, is not strictly true for some ion-combination and oxidation-reduction titrations.

In the titration of very weak acids, for example, the slope of  $\text{pH} = f(V)$  at the equivalent point can be so small that it is difficult to determine the exact point of equivalence with any great degree of accuracy. In these cases it is many times possible to obtain greater accuracy by using various graphical or numerical methods<sup>2</sup>. The most common of these is the plotting of  $\Delta E/\Delta V$  or  $\Delta \text{pH}/\Delta V$  as a function of  $V^{1a}$ . In this method only a few points in the immediate vicinity of the equivalent point are of any significance. With ions of different charges the curve becomes asymmetrical, and the maximum is slightly displaced from the theoretical equivalent point<sup>1b,3a</sup> as shown in Fig. 7.

If  $\Delta V/\Delta E$  or  $\Delta V/\Delta \text{pH}$ , instead of  $\Delta E/\Delta V$  or  $\Delta \text{pH}/\Delta V$ , is plotted against  $V$ , certain advantages are obtained. Such curves are shown in Figs. 3 to 10. It will be noticed that, in the vicinity of the equivalent point, the curves consist of two straight lines which intersect each other and the  $V$ -axis at the equivalent point. The fact that the lines intersect on the  $V$ -axis can be of great importance in cases where ideal curves are not obtained, *e. g.* in precipitation reactions in systems with relatively high solubility products. The slopes of the lines are also of importance. In the titration of ions of similar charge, the curves are generally almost symmetrical about the equivalent point. In most reactions of ions of different charges, the slopes of the two lines are not the same.

If the curve  $\Delta V/\Delta E = f(V)$  is plotted during the actual titration, the approximate position of the end point can generally be estimated long before it is reached and the increments ( $\Delta V$ ) accordingly reduced.

Under some conditions a deviation from the straight lines is found just at the end point. If the straight lines, however, are extrapolated, they will intersect on the  $V$ -axis. A comparison of the  $\Delta E/\Delta V$  and  $\Delta V/\Delta E$  curves for a precipitation titration is shown in Fig. 7. As can be seen, the  $\Delta E/\Delta V$  curve deviates by about 1 %, while the  $\Delta V/\Delta E$  lines intersect at the theoretical equivalent point.

### THEORY

The theoretical background of the above discussion will be outlined in the following section.

#### Neutralization titrations

1. *Strong acid — strong base.* If  $V_0$  ml of a strong acid, with original concentration  $C_A$ , are titrated with a strong base, of concentration  $C_B$ , the concentration of hydrogen ions, after the addition of  $V$  ml of base, will be:

$$C_{H^+} = C_A \frac{V_0}{V_0 + V} - C_B \frac{V}{V_0 + V} \quad (1)$$

pH is defined by:

$$\text{pH} = -\log a_{H^+} = -\log f_+ \cdot C_{H^+} \quad (2)$$

where  $a_{H^+}$  is the hydrogen ion activity and  $f_+$  is the activity coefficient. As the ion strength is scarcely altered during a titration,  $f_+$  may be considered constant and (2) can be written:

$$\text{pH} = k - \log C_{H^+} \quad (3)$$

where  $k = -\log f_+$ . (1) and (3) together give:

$$\text{pH} = k - \log \left( C_A \frac{V_0}{V_0 + V} - C_B \frac{V}{V_0 + V} \right) \quad (4)$$

which is differentiated with respect to pH and  $V$  to give:

$$\frac{dV}{dpH} = \ln 10 \cdot \frac{V_0 + V}{V_0} \cdot \frac{C_A V_0 - C_B V}{C_A + C_B} \quad (5)$$

If the volume of base added at the equivalent point is  $V_e$ ,

$$C_A V_0 = C_B V_e \quad (6)$$

and (5) can be rewritten to give:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V}{V_o + V_e} (V_e - V) \quad (7)$$

In the vicinity of the equivalent point,  $V_o + V$  is approximately equal to  $V_o + V_e$  and (7) is approximated by:

$$\frac{dV}{dpH} = 2.30 \cdot (V_e - V) \quad (8)$$

which is the equation of a straight line, intersecting the  $V$ -axis at  $V = V_e$ .

When the equivalent point has been exceeded in the titration,

$$C_{OH^-} = C_B \frac{V}{V_o + V} - C_A \frac{V_o}{V_o + V} \quad (9)$$

pH is here defined by:

$$pH = pK_w + \log a_{OH^-} = pK_w + \log f_- \cdot C_{OH^-} \quad (10)$$

As  $f_-$  will change only to a very small extent during a titration,  $\log f_-$  may be considered constant and (10) can be written:

$$pH = k_1 + \log \left( C_B \frac{V}{V_o + V} - C_A \frac{V_o}{V_o + V} \right) \quad (11)$$

where  $k_1 = pK_w + \log f_-$ . Differentiation and simplification give:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V}{V_o + V_e} (V - V_e) \quad (12)$$

which, in the vicinity of the equivalent point, can be approximated by:

$$\frac{dV}{dpH} = 2.30 \cdot (V - V_e) \quad (13)$$

The  $dV/dpH$  curves will not be straight lines, if the dilution can not be neglected. If, however,  $\frac{dV/dpH}{V_o + V}$  is calculated instead of  $dV/dpH$ , the curves are transformed to straight lines, as can be seen from the following expressions:

$$\frac{dV/dpH}{V_o + V} = \frac{2.30}{V_o + V_e} (V_e - V) \quad (14)$$

and

$$\frac{dV/dpH}{V_o + V} = \frac{2.30}{V_o + V_e} (V - V_e) \quad (15)$$

where  $V_o + V$  is equal to the total volume of the reaction solution.

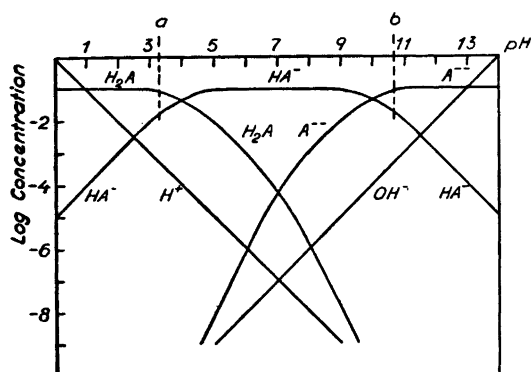


Fig. 1. Logarithmic diagram for a dibasic, weak acid.

2. *Weak acid — strong base.* Formulas will here be derived for weak, dibasic acids with such values of  $pk'_a$  and  $pk''_a$  that  $C_{H^+}$  and  $C_{OH^-}$  can be neglected in comparison to other terms in the range a to b in Fig. 1.

$V_o$  ml of a weak acid ( $H_2A$ ), with original concentration  $C_A$ , are titrated with a strong base of concentration  $C_B$ . For weak acids:

$$pH = pk_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} \quad (16)$$

After the addition of  $V$  ml of base:

$$C_{H_2A} = C_A \frac{V_o}{V_o + V} - C_B \frac{V}{V_o + V} \quad (17)$$

and

$$C_{HA^-} = C_B \frac{V}{V_o + V} \quad (18)$$

Therefore, from (16), (17), and (18):

$$pH = pk'_a + \log \frac{C_A V_o - C_B V}{C_B V} \quad (19)$$

Differentiation and simplification give:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V}{V_e} (V_e - V) \quad (20)$$

In the vicinity of the equivalent point, (20) can be approximated by:

$$\frac{dV}{dpH} = 2.30 \cdot (V_e - V) \quad (21)$$

After the equivalent point has been exceeded ( $V_e < V < 2V_e$ ):

$$C_{HA^-} = 2C_A \frac{V_o}{V_o + V} - C_B \frac{V}{V_o + V} \quad (22)$$

and

$$C_{A^{--}} = C_B \frac{V}{V_o + V} - C_A \frac{V_o}{V_o + V} \quad (23)$$

(22) and (23) together with (16) give:

$$\text{pH} = \text{pk}_a'' + \log \frac{C_B V - C_A V_o}{2C_A V_o - C_B V} \quad (24)$$

which can be differentiated and simplified to:

$$\frac{dV}{d\text{pH}} = 2.30 \cdot \frac{2V_e - V}{V_e} (V - V_e) \quad (25)$$

In the vicinity of the equivalent point, (25) can be approximated by:

$$\frac{dV}{d\text{pH}} = 2.30 \cdot (V - V_e) \quad (26)$$

Equations (7), (12), (20), and (25) are parabolic functions of  $V$ . In the vicinity of the equivalent point, they approximate straight lines. Equations (7) and (12) were transformed to straight lines by dividing by  $V_o + V$  (equations (14) and (15)). In a similar manner, (20) and (25) can be transformed to straight lines by dividing by  $V$  and  $(2V_e - V)$ , respectively:

$$\frac{dV/d\text{pH}}{V} = \frac{2.30}{V_e} \cdot (V_e - V) \quad (27)$$

$$\frac{dV/d\text{pH}}{2V_e - V} = \frac{2.30}{V_e} \cdot (V - V_e) \quad (28)$$

The value of  $2V_e$ , in the denominator in (28), can be obtained with sufficient accuracy from the intersection between (21) or (27) and the  $V$ -axis.

Near the second equivalent point, (25) can be written:

$$\frac{dV}{d\text{pH}} = 2.30 \cdot \frac{V - V_e}{V_e} \cdot (2V_e - V) \quad (29)$$

which, in the vicinity of the equivalent point, can be approximated by:

$$\frac{dV}{d\text{pH}} = 2.30 \cdot (2V_e - V) \quad (30)$$

By dividing  $dV/d\text{pH}$  by  $(V - V_e)$ , (29) is transformed to a straight line:

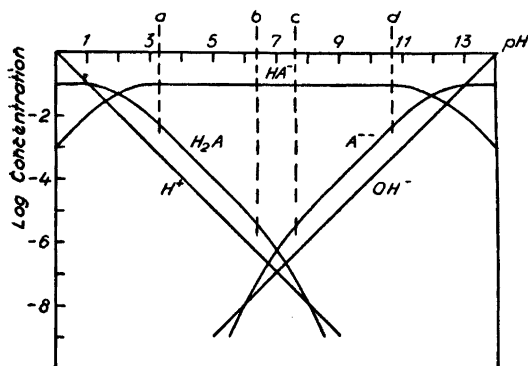


Fig. 2. Logarithmic diagram for a dibasic acid of intermediate strength.

$$\frac{dV/dpH}{V - V_e} = \frac{2.30}{V_e} \cdot (2V_e - V) \quad (31)$$

After exceeding the second equivalent point, equations (12), (13), and (15) should be used.

If the weak acids have such  $pK_a$ -values that their logarithmic diagrams are of the type shown in Fig. 2, the hydrogen and hydroxyl ion concentrations can not be neglected in comparison to the other terms, and it can not be conveniently demonstrated that  $dV/dpH$  is a simple function of  $V$ . However, a demonstration can be made from the expression for the buffer capacity<sup>4</sup>,  $\beta$ . If the titration is made with a strong base, *e. g.* sodium hydroxide,

$$\beta = \frac{dC_{Na+}}{dpH} = 2.30 \cdot (C_{H+} + C_{OH-} + \frac{C_a \cdot C_s}{C}) \quad (32)$$

where, in the range a to b in Fig. 2,  $C$  is the total concentration of the weak acid,  $C_a$  is the concentration of undissociated  $H_2A$ , and  $C_s$  is the concentration of  $HA^-$ .

In the range a to b,  $C_{HA-}$  is approximately equal to  $C$ , and  $C_{OH-}$  and  $C_{A--}$  can be neglected in comparison to  $C_{H+}$  and  $C_{H_2A}$ . Therefore, (32) can be simplified to:

$$\frac{dC_{Na+}}{dpH} = 2.30 \cdot (C_{H+} + C_{H_2A}) \quad (33)$$

Under the same conditions, from:

$$C_{H_2A} = C - C_{HA-} - C_{A--} \quad (34)$$

and the expression for the electro-neutrality conditions in the solution:

$$C_{H+} + C_{Na+} = C_{HA-} + 2C_{A--} + C_{OH-} \quad (35)$$

the following expression can be derived:

$$C_{H+} + C_{H_2A} = C - C_{Na+} \quad (36)$$

which, together with (33), gives:

$$\frac{dC_{\text{Na}^+}}{dpH} = 2.30 \cdot (C - C_{\text{Na}^+}) \quad (37)$$

Using the same terminology as above,

$$C = C_A \cdot \frac{V_o}{V_o + V}, \quad (38)$$

$$C_{\text{Na}^+} = C_B \cdot \frac{V}{V_o + V}, \quad (39)$$

and

$$dC_{\text{Na}^+} = C_B \cdot \frac{V_o}{(V_o + V)^2} \cdot dV \quad (40)$$

The last four equations give, after simplification:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V}{V_o} \cdot (V_e - V) \quad (41)$$

which, in the vicinity of the equivalent point, can be approximated by:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V_e}{V_o} (V_e - V) \quad (42)$$

which shows that  $dV/dpH$  approximates a straight line.  $\frac{dV/dpH}{V_o + V}$  will be a straight-line function of  $V$ , as can be seen from the expression:

$$\frac{dV/dpH}{V_o + V} = \frac{2.30}{V_o} \cdot (V_e - V) \quad (43)$$

In the range c to d in Fig. 2,  $C_{\text{HA}^-}$  is approximately equal to  $C$ , and  $C_{\text{H}_2\text{A}}$  and  $C_{\text{H}^+}$  can be neglected in comparison to the other terms. Therefore, (32) can be simplified to:

$$\frac{dC_{\text{Na}^+}}{dpH} = 2.30 \cdot (C_{\text{A}^{--}} + C_{\text{OH}^-}) \quad (44)$$

Under these conditions, it can be deduced from (34) and (35) that:

$$C_{\text{A}^{--}} + C_{\text{OH}^-} = C_{\text{Na}^+} - C \quad (45)$$

which, together with (44), gives:

$$\frac{dC_{\text{Na}^+}}{dpH} = 2.30 \cdot (C_{\text{Na}^+} - C) \quad (46)$$

This equation, together with (38), (39), and (40), gives:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V}{V_o} \cdot (V - V_e) \quad (47)$$

which, in the vicinity of the equivalent point, can be approximated by:

$$\frac{dV}{dpH} = 2.30 \cdot \frac{V_o + V_e}{V_o} \cdot (V - V_e) \quad (48)$$

to show that  $dV/dpH$  very nearly approximates a straight line. As before, the  $dV/dpH$  curve is transformed to a straight line by dividing by  $(V_o + V)$ :

$$\frac{dV/dpH}{V_o + V} = \frac{2.30}{V_o} \cdot (V - V_e) \quad (49)$$

It should be noticed that formulas (41), (42), (43), (47), (48), and (49) are derived only for a range in the vicinity of the equivalent point. As shall be shown later experimentally, the curves will be straight lines within a rather large range.

#### Ion-combination titrations

1. *Precipitation titrations.* When  $V_o$  ml of a solution of a substance (A), with original concentration  $C_{A_0}$ , are titrated with a solution of a substance (B), of concentration  $C_{B_0}$ , a precipitate ( $A_xB_y$ ) is formed according to the reaction:



As long as A is present in excess:

$$C_A = C_{A_0} \cdot \frac{V_o}{V_o + V} - \frac{x}{y} \cdot C_{B_0} \cdot \frac{V}{V_o + V} \quad (51)$$

where  $V$  is the volume of solution B added. (51) and

$$C_A^x C_B^y = S \quad (52)$$

together give:

$$C_B = \frac{S^{\frac{1}{y}}}{\left(C_{A_0} \cdot \frac{V_o}{V_o + V} - \frac{x}{y} \cdot C_{B_0} \cdot \frac{V}{V_o + V}\right)^{\frac{x}{y}}} \quad (53)$$

At the equivalent point,  $V$  is equal to  $V_e$ , and

$$yC_{A_0} \cdot V_o = xC_{B_0} \cdot V_e \quad (54)$$

(53), after taking logarithms and differentiating, gives:



$$\frac{dV}{d\ln C_B} = \frac{y}{x} \cdot \frac{V_o + V}{V_o + V_e} \cdot (V_e - V) \quad (55)$$

$d\ln C_B$  can be substituted according to:

$$d\ln C_B = \frac{n_B \cdot F}{RT} \cdot dE \quad (56)$$

where  $n_B$  is obtained from the following formula:

$$B_{ox} = B_{red} + n_B e^- \quad (57)$$

Equation (55) can be written:

$$\frac{dV}{dE} = \frac{y}{x} \cdot \frac{n_B \cdot F}{RT} \cdot \frac{V_o + V}{V_o + V_e} \cdot (V_e - V) \quad (58)$$

After the equivalent point has been exceeded, B is present in excess, and

$$C_B = C_{B_o} \cdot \frac{V}{V_o + V} - \frac{y}{x} \cdot C_{A_o} \cdot \frac{V_o}{V_o + V} \quad (59)$$

Taking logarithms, differentiating, and inserting (56) gives:

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot \frac{V_o + V}{V_o + V_e} \cdot (V - V_e) \quad (60)$$

Near the equivalent point, (58) and (60) can be approximated by:

$$\frac{dV}{dE} = \frac{y}{x} \cdot \frac{n_B \cdot F}{RT} \cdot (V_e - V) \quad (61)$$

and

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot (V - V_e) \quad (62)$$

respectively. By dividing (58) and (60) by  $(V_o + V)$  straight-line functions of  $V$  are obtained:

$$\frac{dV/dE}{V_o + V} = \frac{y}{x} \cdot \frac{n_B \cdot F}{RT} \cdot \frac{V_e - V}{V_o + V_e} \quad (63)$$

$$\frac{dV/dE}{V_o + V} = \frac{n_B \cdot F}{RT} \cdot \frac{V - V_e}{V_o + V_e} \quad (64)$$

It can be seen that precipitation titrations are very similar to titrations of strong acids with strong bases.

2. *Complex-formation titrations.* When  $V_0$  ml of a solution of a substance (A), with original concentration  $C_{A_0}$ , are titrated with a solution of a substance (B), of concentration  $C_{B_0}$ , a complex is formed according to the reaction:



This reaction is governed by the complex-constant  $K_c$ , defined by:

$$\frac{C_A^x \cdot C_B^y}{C_{A_x B_y}} = K_c \quad (66)$$

As long as A is present in excess,

$$C_A = C_{A_0} \cdot \frac{V_0}{V_0 + V} - \frac{x}{y} \cdot C_{B_0} \cdot \frac{V}{V_0 + V}, \quad (67)$$

$$C_{A_x B_y} = \frac{1}{y} \cdot C_{B_0} \cdot \frac{V}{V_0 + V}, \quad (68)$$

and

$$C_B^y = K_c \cdot \frac{\frac{1}{y} \cdot C_{B_0} \cdot \frac{V}{V_0 + V}}{\left( C_{A_0} \cdot \frac{V_0}{V_0 + V} - \frac{x}{y} \cdot C_{B_0} \cdot \frac{V}{V_0 + V} \right)^x} \quad (69)$$

Taking logarithms of (69) and differentiating the expression thus obtained gives, together with (56):

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot \frac{yV \cdot (V_0 + V) \cdot (V_e - V)}{V_0 \cdot (V_e - V) + xV \cdot (V_0 + V_e)} \quad (70)$$

If  $x = y = 1$ , (70) can be simplified to:

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot \frac{V}{V_e} \cdot (V_e - V) \quad (71)$$

in full agreement with (20).

Compared to similar equations for the previous systems, (70) is rather complicated. However, in the vicinity of the equivalent point,  $V_0 \cdot (V_e - V)$  can be neglected in comparison to  $xV \cdot (V_0 + V_e)$ . Therefore (70) can be approximated by:

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot \frac{y}{x} \cdot (V_e - V) \quad (72)$$

After the equivalent point has been exceeded, B is present in excess, and

$$C_B = C_{B_0} \cdot \frac{V}{V_0 + V} - \frac{y}{x} \cdot C_{A_0} \cdot \frac{V_0}{V_0 + V} \quad (73)$$

This, after taking logarithms and differentiating, gives, together with (56):

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot \frac{V_o + V}{V_o + V_e} \cdot (V - V_e) \quad (74)$$

This expression is of the strong acid — strong base type and can, in the vicinity of the equivalent point, be approximated by:

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot (V - V_e) \quad (75)$$

By dividing  $dV/dE$  by  $(V_o + V)$  in the usual manner, a straight-line function of  $V$  is obtained:

$$\frac{dV/dE}{V_o + V} = \frac{n_B \cdot F}{RT} \cdot \frac{V - V_e}{V_o + V_e} \quad (76)$$

#### Oxidation-reduction titrations

When  $V_o$  ml of a solution of a substance (A) in its reduced state, with original concentration  $C_A$ , are titrated with a solution of a substance (B) in its oxidized state, of concentration  $C_B$ , the following reactions take place in the solution:

$$A_{\text{red}} = A_{\text{ox}} + n_A e^- \quad (77)$$

and

$$B_{\text{ox}} + n_B e^- = B_{\text{red}} \quad (78)$$

When  $V$  ml of solution B has been added

$$C_{A_{\text{ox}}} = \frac{n_B}{n_A} \cdot C_B \cdot \frac{V}{V_o + V} \quad (79)$$

and

$$C_{A_{\text{red}}} = C_A \cdot \frac{V_o}{V_o + V} - \frac{n_B}{n_A} \cdot C_B \cdot \frac{V}{V_o + V} \quad (80)$$

The potential in the solution is governed by:

$$E = e_A^o + \frac{RT}{n_A \cdot F} \cdot \ln \frac{C_{A_{\text{ox}}}}{C_{A_{\text{red}}}} \quad (81)$$

Inserting (79) and (80) in (81), taking logarithms, and differentiating the resulting expression gives:

$$\frac{dV}{dE} = \frac{n_A \cdot F}{RT} \cdot \frac{V}{V_e} \cdot (V_e - V) \quad (82)$$

which is of the weak acid — strong base type. In the vicinity of the equivalent point, it can be approximated by:

$$\frac{dV}{dE} = \frac{n_A \cdot F}{RT} \cdot (V_e - V) \quad (83)$$

By dividing  $dV/dE$  by  $V$  a straight-line function of  $V$  is obtained:

$$\frac{dV/dE}{V} = \frac{n_A \cdot F}{RT} \cdot \frac{V_e - V}{V_e} \quad (84)$$

When the equivalent point has been exceeded

$$C_{B_{red}} = \frac{n_A}{n_B} \cdot C_A \cdot \frac{V_o}{V_o + V} \quad (85)$$

and

$$C_{B_{ox}} = C_B \cdot \frac{V}{V_o + V} - \frac{n_A}{n_B} \cdot C_A \cdot \frac{V_o}{V_o + V} \quad (86)$$

The potential is determined by:

$$E = e_B^o + \frac{RT}{n_B \cdot F} \ln \frac{C_{B_{ox}}}{C_{B_{red}}} \quad (87)$$

(85) and (86) are inserted in (87). Taking logarithms and differentiating give:

$$\frac{dV}{dE} = \frac{n_B \cdot F}{RT} \cdot (V - V_e) \quad (88)$$

which will be a straight line under all conditions.

#### THE INCREMENT $\Delta V$

The formulas in the preceeding section have been derived for infinitely small increments,  $\Delta V$ . In practice it is, of course, impossible to make the increments infinitely small. It is therefore necessary to calculate in as simple a manner as possible the values of  $V$  against which  $\Delta V/\Delta pH$  or  $\Delta V/\Delta E$  should be plotted. If  $\Delta V$  is not too large, no great error ensues, if  $\Delta V/\Delta pH$  or  $\Delta V/\Delta E$  is plotted against  $V + \frac{1}{2}\Delta V$ . For greater values of  $\Delta V$  it may be necessary to make a correction.  $\Delta V/\Delta pH$  or  $\Delta V/\Delta E$  is then plotted against  $V + c\frac{1}{2}\Delta V$ . The correction factor ( $c$ ) is determined by the ratio between  $\Delta V$  and the absolute value of  $V_e - V$ . In Table 1 the factor  $c$  is shown as a function of the ratio  $\Delta V/|V_e - V|$ .

Table 1. Correction factor  $c$  as a function of the ratio  $\Delta V/|V_e - V|$ .

$\frac{\Delta V}{ V_e - V }$	$V_e > V$	$V > V_e$
0.01	1.0016	0.9984
0.02	1.0033	0.9967
0.05	1.0086	0.9914
0.10	1.0176	0.9824
0.15	1.0271	0.9729
0.20	1.0374	0.9626
0.25	1.0480	0.9520
0.30	1.0594	0.9406
0.40	1.0848	0.9152
0.50	1.1146	0.8854
0.60	1.1506	0.8494
0.70	1.1959	0.8041
0.80	1.2573	0.7427
0.90	1.3536	0.6464

In cases where the solution reaches the equilibrium potential very slowly, much time might be saved by making the increments rather large and applying the corrections to the values thus obtained. If  $\Delta V$  is less than about 20 % of  $|V_e - V|$ , there is generally no need to make any corrections. The value of  $V_e$ , which is needed to calculate the factor  $c$ , can be obtained with sufficient accuracy from the titration curve or from the  $\Delta V/\Delta \text{pH}$  or  $\Delta V/\Delta E$  curves, calculated without corrections.

The use of the correction factor is shown in the following example:

50 ml of a strong acid are titrated with a strong base. From the titration curve,  $V_e$  can be estimated to be about 20 ml. If a 3.00 ml increment of reagent was added between  $V = 15.00$  and  $V = 18.00$  ml, the pH-values obtained being 2.041 and 2.463 respectively,  $\Delta V$  is about 60 % of  $|V_e - V|$  and therefore the correction factor  $c$  is 1.15.

$$\Delta V/\Delta \text{pH} = 3.00/0.422 = 7.109$$

$$V + c\frac{1}{2}\Delta V = 15.00 + 1.15 \cdot 0.5 \cdot 3.00 = 16.73$$

$$V_o + V + c\frac{1}{2}\Delta V = 50 + 16.73 = 66.73$$

$$\frac{\Delta V/\Delta \text{pH}}{V_o + V + c\frac{1}{2}\Delta V} = \frac{7.109}{66.73} = 0.1065$$

In the  $\Delta V/\Delta \text{pH}$  vs.  $V$  diagram, 0.1065 is plotted against 16.73. Without corrections, 0.1069 would have been plotted against 16.50.

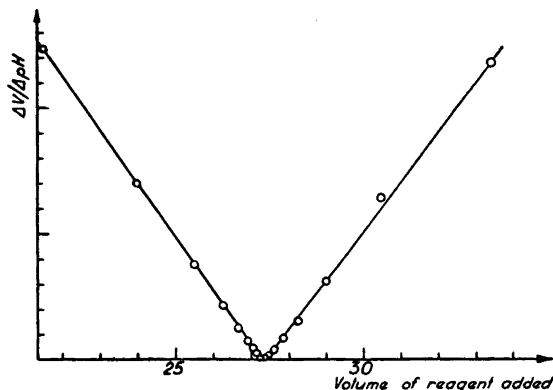


Fig. 3.  $\Delta V/\Delta pH$  curve for the titration of HCl with NaOH.

If the titration had been made on a weak acid instead of on a strong one, the following value should have been calculated:

$$\frac{\Delta V/\Delta pH}{V + c\frac{1}{2}\Delta V} = \frac{7.109}{16.73} = 0.4249$$

and 0.4249 should have been plotted against 16.73. Without corrections 0.4308 would have been plotted against 16.50.

It should be pointed out here that the same formula must be used for the calculation of the entire  $\Delta V/\Delta pH$  or  $\Delta V/\Delta E$  curve. For example, it is not possible to calculate part of the curve using (8) and part using (14), since the values thus obtained differ by a factor of  $(V_o + V_e)$ . If, however, (14) is written:

$$\frac{dV/dpH}{\frac{V_o + V}{V_o + V_e}} = 2.30 \cdot (V_e - V), \quad (14a)$$

(8) and (14 a) can be used for different parts of the curves, *e. g.*, (14 a) for the first part and (8) for the range in the vicinity of the equivalent point.

### EXPERIMENTAL

In the following section some  $\Delta V/\Delta pH$  and  $\Delta V/\Delta E$  curves will be shown. These curves have been obtained in actual titrations using a *Radiometer* potentiometer, type PHM 3f.

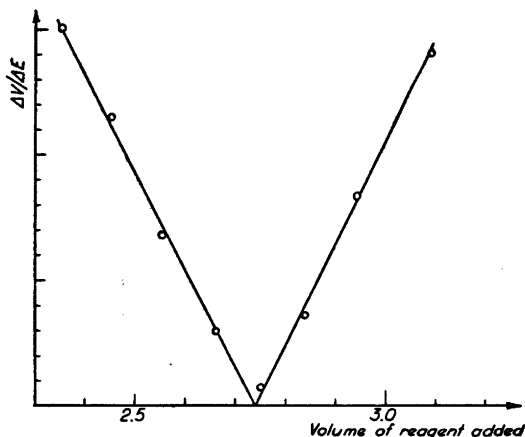


Fig. 4.  $\Delta V/\Delta E$  curve for the titration of benzoic acid in ethylenediamine with an ethylenediamine solution of sodium aminoethoxide.

#### Neutralization titrations

1. *Strong acid — strong base.* 25.00 ml of 0.1087 *N* hydrochloric acid were diluted with distilled water to about 100 ml and titrated with 0.0995 *N* sodium hydroxide solution. The pH of the solution was measured with a glass electrode against a saturated calomel electrode. The data found in Fig. 3 were calculated from the readings using (8) and (13). The pH values above 9 have been corrected with the help of a nomograph supplied with the potentiometer.

2. *Titration of benzoic acid with sodium aminoethoxide in ethylenediamine solution.* 34.40 mg of benzoic acid were dissolved in 40 ml of dry ethylenediamine and titrated with a 0.1029 *N* ethylenediamine solution of sodium aminoethoxide<sup>5</sup>, according to a slightly modified method of Moss, Elliott, and Hall<sup>6</sup>. The measurements were made with an ignited, bright platinum electrode against a calomel electrode with ethylenediamine, saturated with lithium chloride, as solvent<sup>5</sup>. The  $\Delta V/\Delta E$  curve was calculated from (8) and (13) and corrected (see page 572). The curve is shown in Fig. 4.

3. *Weak acid — strong base.* 10.00 ml of 0.1118 *M* phosphoric acid were diluted with distilled water to 150 ml and titrated with 0.0995 *N* sodium hydroxide solution. The pH values were determined by a glass electrode against a saturated calomel electrode. In Fig. 5  $\Delta V/\Delta \text{pH}$  curves, calculated from (42), (26), (21), and (48), are shown (pH values uncorrected). In Fig. 6 are shown  $\Delta V/\Delta \text{pH}$  curves for the same titration calculated from (43), (28), (31), and (49). As can be seen, the parabolic part of the curve in Fig. 5 has been transformed to straight lines.

#### Precipitation titrations

1. *Titration of silver ions with chromate.* 10.00 ml of 0.0999 *N* silver nitrate solution were diluted to 50 ml and titrated with 0.1020 *N* potassium chromate. A silver wire was used as indicator electrode and measurements were made against a calomel electrode with a saturated ammonium nitrate bridge. In Fig. 7 both  $\Delta V/\Delta E$  and  $\Delta E/\Delta V$  curves are shown. As can be seen, the  $\Delta E/\Delta V$  curve reaches a maximum about 1 % before the

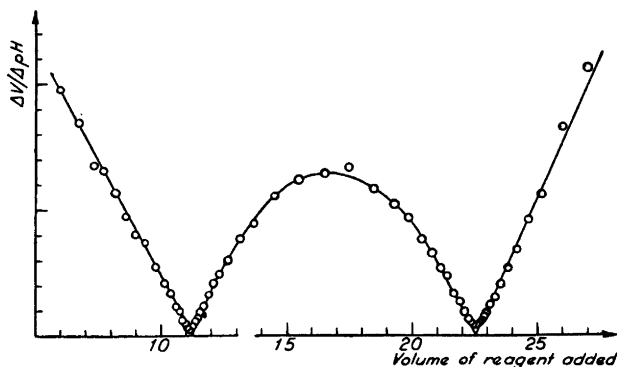


Fig. 5.  $\Delta V/\Delta pH$  curve for the titration of  $H_3PO_4$  with  $NaOH$ .

extrapolated  $\Delta V/\Delta E$  curve reaches its minimum. The value obtained from the  $\Delta V/\Delta E$  curve coincides with the calculated equivalent point.

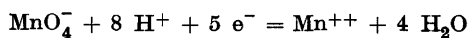
2. *Titration of iodide, bromide, and chloride ions with silver ions.* 10.00 ml of 0.0938 *N* potassium iodide, 10.00 ml of 0.0981 *N* sodium bromide, and 10.00 ml of 0.1087 *N* potassium chloride solutions were mixed and diluted to 100 ml, and 2 grams of ammonium nitrate were added. The solution was titrated with a 0.0999 *N* silver nitrate solution in the same manner as in the preceding experiment. The  $\Delta V/\Delta E$  curves obtained are shown in Fig. 8.

#### Complex-formation titration

To 20.00 ml of 0.1128 *N* potassium cyanide solution, 2 ml of 2 *N* ammonium hydroxide were added. The solution was diluted to 100 ml and titrated with 0.0999 *N* silver nitrate in the same way as before. The  $\Delta V/\Delta E$  curve obtained is shown in Fig. 9. The first part of the curve is not in accordance with the theoretical requirements for the formation of  $Ag(CN)_2^-$  ions, probably due to the fact that ammonium hydroxide was added. Nevertheless, the equivalent point is indicated very sharply.

#### Oxidation-reduction titration

A mixture of 15.00 ml of 0.0914 *N* ferrous sulfate and 5 ml of 5 *N* sulfuric acid were diluted to 100 ml with distilled water and titrated with 0.1009 *N* potassium permanganate solution. Measurements were made with an ignited, bright platinum electrode against a saturated calomel electrode. The  $\Delta V/\Delta E$  curve for the titration is shown in Fig. 10. An enlargement of a section of the curve in the vicinity of the equivalent point is also shown in Fig. 10. It can be seen that the curve is parabolic before and straight after the equivalent point, in full agreement with (82) and (88). The slope of the straight line, however, should have been much greater — about 5 times the slope of the parabolic curve in the vicinity of the equivalent point. The discrepancy is probably due to the fact that the reaction



is not strictly reversible<sup>3b,7</sup>.



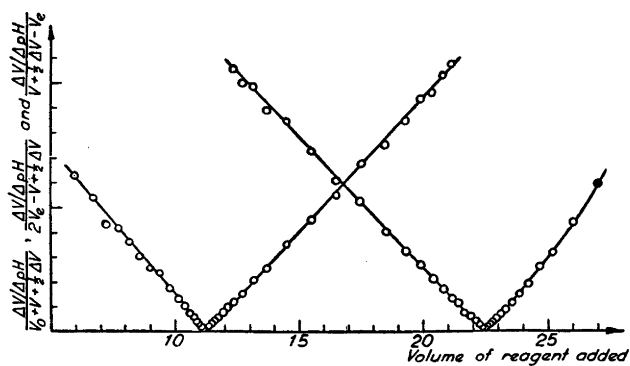


Fig. 6.  $\Delta V/\Delta pH$  curve for the titration of  $H_3PO_4$  with  $NaOH$ . The parabolic part of the curve in Fig. 5 has been transformed to straight lines. (See text.)

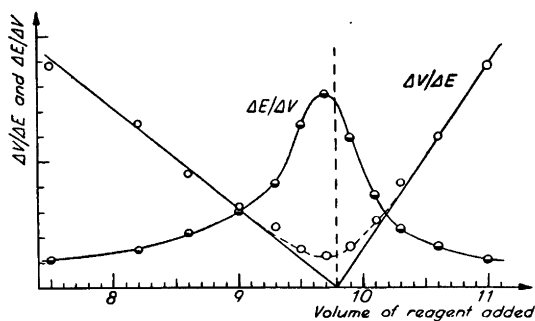


Fig. 7.  $\Delta V/\Delta E$  and  $\Delta E/\Delta V$  curves for the titration of  $Ag^+$  with  $CrO_4^{--}$ .  
 —○—○—  $\Delta V/\Delta E$ ; —●—●—  $\Delta E/\Delta V$ .

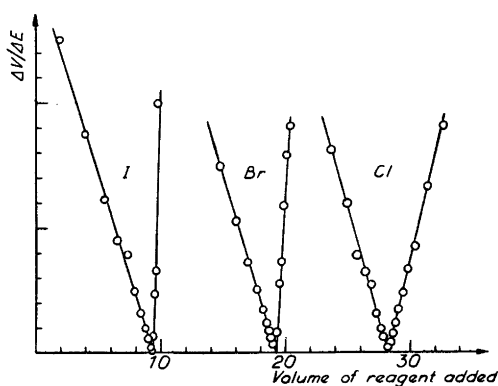


Fig. 8.  $\Delta V/\Delta E$  curves for the titration of  $I^-$ ,  $Br^-$ , and  $Cl^-$  with  $Ag^+$ .

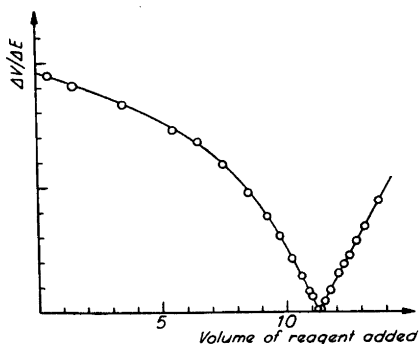


Fig. 9.  $\Delta V/\Delta E$  curve for the titration of  $\text{Ag}^+$  with  $\text{CN}^-$ .

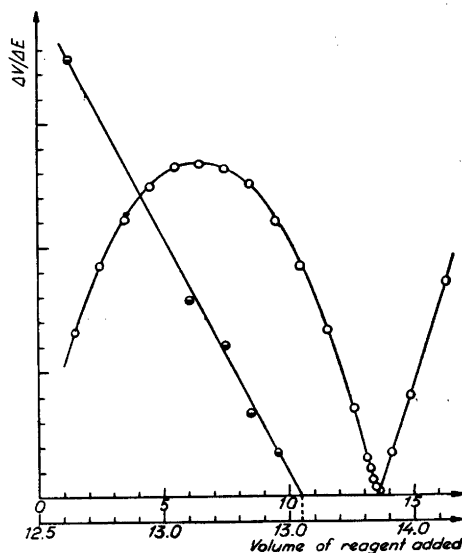


Fig. 10.  $\Delta V/\Delta E$  curves for the titration of  $\text{Fe}^{++}$  with  $\text{MnO}_4^-$ .  
—●— enlarged section of curve.

### SUMMARY

It has been shown that by plotting  $\Delta V/\Delta \text{pH}$  or  $\Delta V/\Delta E$  versus  $V$ , the equivalent point in potentiometric titrations can be determined very accurately. In the vicinity of the equivalent point, the  $\Delta V/\Delta \text{pH}$  and  $\Delta V/\Delta E$  curves are very nearly straight lines. From the appearance of the curves some conclusions can be drawn concerning the reactions taking place during the titration. The application of a correction factor, for use in very accurate work, is discussed. The method has been verified by actual potentiometric titrations of various kinds.

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