CLXXXV.—*A General (Exact) Equation to the Potentiometric-titration Curve.*

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Section 1.

IN a previous paper (Part II; J., 1928, 855) an exact equation was obtained, on thermodynamic grounds, representing the whole potentiometric-titration curve in all cases where (*a*) the analytical reaction consists in the combination of two ions of like valency to form a substance of constant activity such as a precipitate, and (*b*) the indicator electrode behaves as a " soluble electrode " towards either of these ions. Essentially of the tractable form,

$$X = \sinh U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where U and X represent distance from the equivalence point in terms of potential and of quantity of reagent, respectively), this equation was used in developing certain highly refined methods of titration. It will now be shown that both the equation and the methods arising out of it can be generalised. A system involving both analytical and electrode reactions of the most general type yields, under equilibrium conditions, a titration curve exactly represented by an equation of the form

$$X = \underset{\alpha\beta}{\sinh} U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\underset{\alpha\beta}{\sinh} U = \tfrac{1}{2}(e^{\alpha U} - e^{-\beta U}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)^*$$

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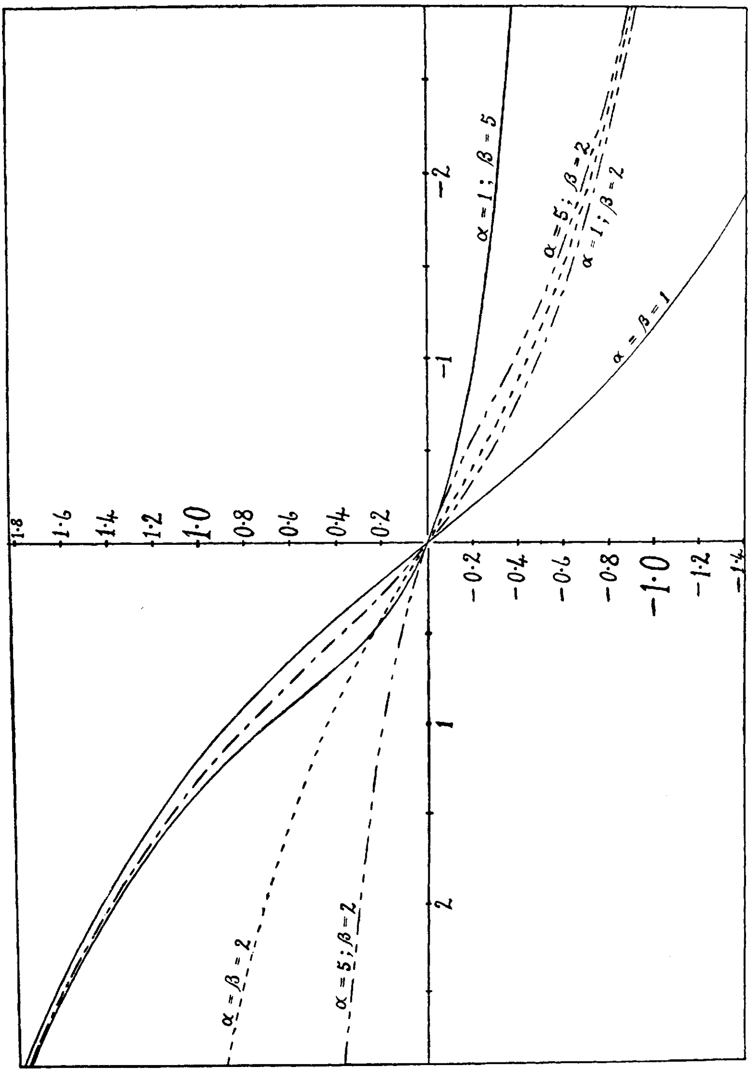
* This equation could be written in the form $\underset{\alpha\beta}{\sinh} U = e^{\frac{\alpha-\beta}{2}U} \sinh \frac{\alpha+\beta}{2}U$, and similarly for other hyperbolic functions of U, but the formulæ would be, not only cumbersome, but less direct in their physicochemical significance.

FIG. 1.

Typical forms of the curve represented by the general titration-curve equation. (*Graphs of the function* $X = \sinh_{\alpha\beta} U$ *for various assigned values of the parameters* α *and* β.)

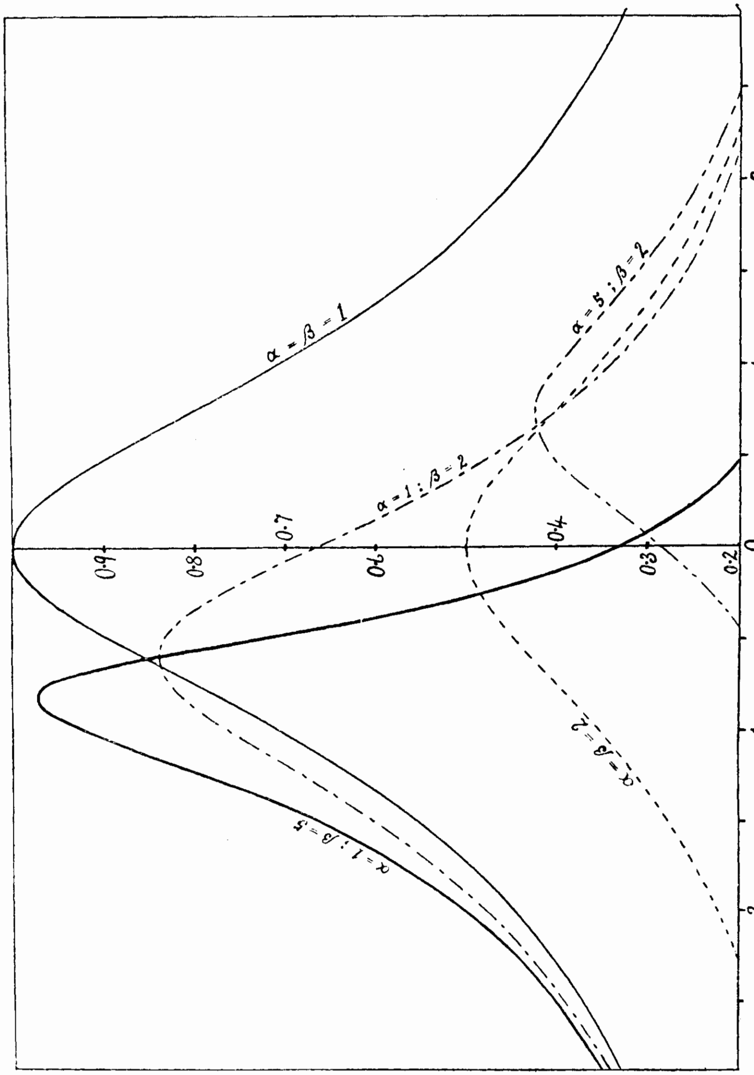


The origin represents the point of exact equivalence. Abscissæ (X) represent distance from the equivalence point in terms of quantity of reagent solution, the unit being H c.c. (see Section 2). Ordinates (U) represent distance from the equivalence point in terms of potential, the unit being RT/F (*i.e.*, about 25 millivolts). Three kinds of broken line are used to distinguish the curves.

and α and β are two simple numbers characteristic of the system (see Section 3, and Fig. 1).

Between the function defined in (3) and the corresponding cosine and other functions (see Section 4) many of the inter-relations of the ordinary hyperbolic functions hold good (for fixed values of α and β), while others assume a more general form. These relations facilitate the derivation of methods of refined titration essentially

FIG. 2. Derived curves, corresponding with those of *Fig.* 1. [*Graphs of the function* h^{-1} *sech*$_{\alpha\beta}$ (g + *arcsinh* X), i.e., *of* h^{-1} *sech*$_{\alpha\beta}$ (g + U).]



Abscissæ (X) correspond exactly with those of Fig. 1. Ordinates represent rate of change of potential, dU/dX (*i.e.*, the slope of the corresponding curve in Fig. 1), the unit being RT/FH, or about $25/H$ millivolts/c.c.

similar to those already described, but with the advantage of general applicability.

By means of these methods, not only is the sensitivity, or absolute precision, obtainable from the accepted reactions very much increased, but also other reactions should become available for analytical purposes which otherwise would not be sufficiently sensitive. Incidentally the same methods also provide an accurate means of determining equivalence-point potentials and reaction constants (compare Part II, p. 870).

The rigorous deduction of the general titration-curve equation appears to be especially useful in providing a sound basis for the quantitative study of all the various analytical and electrode reactions that are now available or may yet be discovered. In so far as such study is to be anything more than mere empiricism, it must rest upon the assumption and the attempted realisation of equilibrium conditions, and this is the only assumption on which the following deduction is based.

Section 2. *Deduction of the Equation.*

This deduction may be effected concisely and yet with strict generality by adopting the device of writing the chemical and thermodynamic equations in an algebraic manner, such that no formal distinction need be made between products of the reactions and reactants other than the two principal reactants. Four abstract or typical molecular symbols will then suffice to represent all possibilities, whereas otherwise eight at least would be necessary. The procedure at this stage may be illustrated by a concrete case.

The reduction of iodate ion by (aqueous) sulphur dioxide in strongly acid solution has recently been studied potentiometrically (Hendrixson, *J. Amer. Chem. Soc.*, 1925, **47**, 1319; the author actually used a solution of sodium sulphite, but in effect this was the same as adding aqueous sulphur dioxide, since a large excess of acid was present), and shown to proceed in two clearly separated stages. Considering only the first of these, the analytical reaction is

$$2IO_3' + 5SO_2 + 4H_2O = I_2 + 5SO_4'' + 8H^{\cdot} \quad . \quad . \quad (4)$$

Iodate ion and sulphur dioxide are the two principal reactants; the latter, being the added substance, may conveniently be called the "reagent," and the former the "titrated substance." In order to avoid needless repetition, the word "substance" will be taken to include ionic or molecular species throughout this paper, and similarly the expression "g.-mol." will cover "g.-ion."

Before the first addition of reagent, the only electrode reaction is

$$10\ominus + 2IO_3' + 12H^{\cdot} = I_2 + 6H_2O \quad . \quad . \quad . \quad (5)$$

(where the symbol $\ominus$ represents one faraday of negative electricity), but when once the titration has commenced there is the alternative electrode reaction

$$-10\ominus + 5SO_2 + 10H_2O = 5SO_4'' + 20H^{\cdot} \quad . \quad . \quad (6)$$

obtained by subtracting (5) from (4). These equations must now be re-written in the algebraic manner convenient for the present purpose by transferring the symbols of the " subsidiary reactants," *i.e.*, all save the two principal reactants, to the right-hand sides with change of sign, thus :

$$10\ominus + 2IO_3' = I_2 - 12H^{\cdot} + 6H_2O \quad . \quad . \quad . \quad . \quad (7)$$

$$-10\ominus + 5SO_2 = 5SO_4'' + 20H^{\cdot} - 10H_2O \quad . \quad . \quad . \quad (8)$$

$$2IO_3' + 5SO_2 = I_2 + 5SO_4'' + 8H^{\cdot} - 4H_2O \quad . \quad . \quad (9)$$

and the corresponding thermodynamic equations (for equilibrium) can be written logarithmically in an entirely parallel manner, the algebraic signs being retained.

We now revert to the general treatment. Representing the molecular or ionic symbols (in the abstract) by capital letters, and taking A as the titrated substance, and B as the reagent, we express the alternative electrode reactions quite generally by the equations

$$\pm\nu\ominus + a\mathrm{A} = \Sigma p\mathrm{P} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\mp\nu\ominus + b\mathrm{B} = \Sigma q\mathrm{Q} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the small letters representing numerical coefficients, of which those on the right, typified by p and q, may be either positive or negative as in equations (7) and (8). From the latter it is also seen that the symbols represented by P, Q, etc., are not necessarily all different. The equation for the analytical reaction is obtained from (10) and (11) by addition, giving

$$a\mathrm{A} + b\mathrm{B} = \Sigma p\mathrm{P} + \Sigma q\mathrm{Q} \quad . \quad . \quad . \quad . \quad (12)$$

and the three thermodynamic equations corresponding to (10), (11), (12), respectively, are then written in terms of the equivalent concentrations C_{A}, C_{B}, etc., the activity coefficients γ_{A}, γ_{B}, etc., and the measured potential E. It is convenient to adopt the convention that *the direction in which* E *changes during titration is taken as the negative direction*, thus avoiding alternative signs, and we have

$$\nu F/RT\,.\,(E_0 - E) + a \log C_{\mathrm{A}}\gamma_{\mathrm{A}} = \Sigma p \log C_{\mathrm{P}}\gamma_{\mathrm{P}} \quad . \quad . \quad . \quad (13)$$

$$-\nu F/RT\,.\,(E'_0 - E) + b \log C_{\mathrm{B}}\gamma_{\mathrm{B}} = \Sigma q \log C_{\mathrm{Q}}\gamma_{\mathrm{Q}} \quad . \quad . \quad . \quad (14)$$

$$-\log K + a \log C_{\mathrm{A}}\gamma_{\mathrm{A}} + b \log C_{\mathrm{B}}\gamma_{\mathrm{B}} = \Sigma p \log C_{\mathrm{P}}\gamma_{\mathrm{P}} + \Sigma q \log C_{\mathrm{Q}}\gamma_{\mathrm{Q}} \quad . \quad . \quad (15)$$

in which logarithms (as throughout this paper) are to the base e; F, R, and T have their usual significance; and the three constants, E_0, E'_0, and K, are connected by the relation

$$\log K = \nu F/RT\,.\,(E'_0 - E_0) \quad . \quad . \quad . \quad . \quad (16)$$

These equations express the assumption of equilibrium conditions.

Now suppose (as in Part I, J., 1928, 843, and Part II, *loc. cit.*) that at any given stage of the titration, M c.c. of the reagent solution are still required in order to reach the exact equivalence point. Thus M may be positive or negative, but in any case, to know M is, from the experimental point of view, to know the result of the titration. If n is the normality of the reagent solution (which may or may not be known) then the excess of the titrated substance at this stage is evidently Mn mg.-equivs.*

In order to show how adsorption by precipitates (if any) would affect the titration curve, a coefficient, θ_A, is now introduced, representing the ratio of the amount of A present in solution (*i.e.*, not adsorbed) to the total amount present (compare Part I, p. 848); a similar coefficient, θ_B, relates to B.

Then if V c.c. is the volume of the solution at this stage, the total amount (mg.-equivs.) of A in the vessel is VC_A/θ_A, and similarly that of B is VC_B/θ_B, and since the excess of A is Mn mg.-equivs.,

$$Mn = VC_A/\theta_A - VC_B/\theta_B \quad . \quad . \quad . \quad . \quad (17)$$

The remaining steps, by which C_A and C_B are eliminated and the result is reduced to a tractable form, will be plain if three constants α, β, $\bar{E}_0$, and two other quantities, H and G (not in general constant, but independent of C_A and C_B), are first defined by the equations

$$a\alpha = b\beta = \nu$$

$$(\alpha + \beta)\bar{E}_0 = \alpha E_0 + \beta E'_0 \quad . \quad . \quad . \quad . \quad (18)$$

$$(\alpha + \beta)G = \log(\gamma_B\theta_B/\gamma_A\theta_A) + \Sigma\frac{p}{a}\log C_P\gamma_P - \Sigma\frac{q}{b}\log C_Q\gamma_Q \quad . \quad (19)$$

$$(a + b)\log(nH/2V) = \log K - a\log\gamma_A\theta_A - b\log\gamma_B\theta_B + \Sigma p\log C_P\gamma_P + \Sigma q\log C_Q\gamma_Q \quad . \quad . \quad . \quad . \quad (20)$$

Then, from equations (13), (14), (15), and (17), the general titration-curve equation connecting M and E is obtained in the form

$$M/H = \sinh_{\alpha\beta}[(F/RT)(E - \bar{E}_0) + G] \quad . \quad . \quad . \quad (21)$$

and, since this is identical with equation (2),

$$X = M/H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$U = (F/RT).(E - \bar{E}_0) + G \quad . \quad . \quad . \quad . \quad (23)$$

From equations (19) and (20), G and H are seen to depend on the concentrations of the products and subsidiary reactants (if any), the adsorption and activity coefficients, and (in the case of H) the volume of the solution. Their complexity and probable variation might appear, at first sight, to render impracticable the general

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* Ordinary usages have been adhered to as far as possible, but it is plain that the reagent might be measured in other units—in g. of solution, or of the pure substance B, or of some compound of B, etc.—so long as n is defined as the number of mg.-equivs. of B per unit.

application of the equation and of the methods of titration based upon it, but this is not the case. In using these methods, variation in H and G can be accurately allowed for by applying a predetermined additive correction to the measured potentials (see Section 7), after which the procedure is exactly as if H and G were strictly constant during a titration.

The volume H c.c. is, as it were, a " natural " unit-quantity of the reagent solution, in terms of which X represents distance from the equivalence point. Since U vanishes with X (*i.e.*, at the equivalence point),

$$E_e = \bar{E}_0 - RTG_e/F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$U = F(E - E_e)/RT + (G - G_e) \quad . \quad . \quad . \quad (25)$$

where E_e and G_e are the equivalence-point values of E and G. But the difference $(G - G_e)$ is either negligible or is made so by the application of the corrections just mentioned, so that essentially U represents distance from the equivalence point in terms of the unit RT/F (= 25·00 millivolts at 17·0°).

Section 3. *Characteristic Forms of the Titration Curve.*

The Electrode-valencies.—Some examples of the curves represented by the general equation (2), are exhibited in Fig. 1. The intersection of the axes represents the point of exact equivalence, and the positive direction of X is towards the left, so that the progressive addition of the reagent is represented by moving from left to right, as is customary in titration diagrams.

The forms of the curves will be better appreciated when considered in conjunction with the corresponding curves (Fig. 2), in which dU/dX is plotted against X. It is noticeable that the maxima in Fig. 2, and correspondingly the points of inflexion in Fig. 1, do not occur at the equivalence point except in the symmetrical cases where $\alpha = \beta$. Actually (see Section 4) they occur where $(\alpha + \beta)U = 2 \log (\beta/\alpha)$. Any one of the curves in Fig. 1, when rotated about the origin through 180°, coincides with the curve obtained by interchanging α and β.

The parameters α and β, which characterise the curves, are by definition equal to the ratios ν/a and ν/b respectively, and from (13) and (14) it is seen that 1 g.-mol. of the titrated substance " reacts " with ν/a faradays of electricity in one of the electrode reactions, while in the other, 1 g.-mol. of the reagent reacts with ν/b faradays.

For instance, in a precipitation reaction, with an indicator electrode behaving as a " soluble " electrode towards either of the precipitated ions, α and β would be the valencies of the two ions.

More generally, therefore, the term "electrode-valency" may be used to signify the number of faradays of electricity reacting with 1 g.-mol. of a given substance in a particular electrode-reaction. Thus α and β are the electrode-valencies of A and B in this system.

In many cases, though not all, the electrode-valency is simply the ratio of the molecular weight to the equivalent weight ordinarily used in volumetric analysis. For instance, it is 5 for the permanganate ion and 1 for the ferrous ion, with a platinum electrode, the electrode reactions being

$$\left.\begin{aligned} 5\ominus + MnO_4' &= Mn^{\cdot\cdot} + 4H_2O - 8H^{\cdot} \\ -5\ominus + 5Fe^{\cdot\cdot} &= 5Fe^{\cdot\cdot\cdot} \end{aligned}\right\} \quad . \quad . \quad (26a)$$

Similarly, in the iodate titration (p. 1429), equations (7) and (8) show that the electrode-valencies of the two principal reactants, iodate ion and sulphur dioxide, are respectively 5 and 2. On the other hand in Greeff's titration of fluoride ion by ferric ion, as applied potentiometrically by Treadwell and Köhl (*Helv. Chim. Acta*, 1925, **8**, 500), the electrode-valency would not be equal to the ratio of the molecular weight to the ordinarily accepted equivalent weight, for here the alternative electrode reactions are

$$\left.\begin{aligned} \ominus + Fe^{\cdot\cdot\cdot} &= Fe^{\cdot\cdot} \\ -\ominus + 6F' &= (FeF_6)''' - Fe^{\cdot\cdot} \end{aligned}\right\} \quad . \quad . \quad (26b)$$

whence the electrode-valencies of ferric and fluoride ions would be 1 and $\frac{1}{6}$, respectively.

Section 4. *Some Mathematical Properties of the Curves.*

The curves in Fig. 1 are graphs of the function $\underset{\alpha\beta}{\sinh}\, U$ for various assigned values of the parameters α and β. If the positive directions of both axes of co-ordinates are reversed, the curves then represent the complementary function $\underset{\beta\alpha}{\sinh}\, U$, for

$$-\underset{\alpha\beta}{\sinh}\,(-U) = \tfrac{1}{2}(e^{\beta U} - e^{-\alpha U}) = \underset{\beta\alpha}{\sinh}\, U \quad . \quad . \quad (27)$$

Correspondingly, there are two complementary cosine functions,

$$\underset{\alpha\beta}{\cosh}\, U = \underset{\beta\alpha}{\cosh}\,(-U) = \tfrac{1}{2}(e^{\alpha U} + e^{-\beta U}) \quad . \quad . \quad (28)$$

and the other functions are obtained from these according to the usual conventions, *e.g.*, $\underset{\alpha\beta}{\tanh}\, U = \underset{\alpha\beta}{\sinh}\, U/\underset{\alpha\beta}{\cosh}\, U$, and $\underset{\alpha\beta}{\operatorname{sech}}\, U = 1/\underset{\alpha\beta}{\cosh}\, U$.

If, now, the purely numerical constants, $(\alpha^{\beta}\beta^{\alpha})^{1/(\alpha+\beta)}$ and $\frac{1}{\alpha+\beta}\log\left(\frac{\alpha}{\beta}\right)$, are represented by h and g respectively, the first derivative of $\underset{\alpha\beta}{\sinh} U$ (or dX/dU) can be written in the form $h \underset{\alpha\beta}{\cosh} (U + g)$, and it is the reciprocal of this, *i.e.*, dU/dX or $h^{-1} \underset{\alpha\beta}{\operatorname{sech}} (U + g)$, which is plotted against X in Fig. 2. Similarly, the first derivative of $\underset{\alpha\beta}{\cosh} U$ is $h \underset{\alpha\beta}{\sinh} (U + g)$, and it follows that the *second* derivative of $\underset{\alpha\beta}{\sinh} U$ is $h^2 \underset{\alpha\beta}{\sinh} (U + 2g)$. Thus each curve in Fig. 1 has a point of inflexion where $U = -2g$ and $X = -\underset{\beta\alpha}{\sinh} 2g$. This is the point of maximal slope and sensitivity (see Section 9), the maximal value of dU/dX being $h^{-1} \underset{\beta\alpha}{\operatorname{sech}} g$. The following table shows the values of these characteristic constants for several types of curve. In the last column the quantity $50g$ is tabulated, being the distance of the point of inflexion from the equivalence point in millivolts at 17° (*i.e.*, $RT/F \,.\, 2g$).

α.	β.	h.	g.	$-X_{\text{infl.}}$	$\left(\frac{dX}{dU}\right)_{\text{min.}}$	$\left(\frac{dU}{dX}\right)_{\text{max.}}$	$E_e - E_{\text{infl.}}$
1	1	1	0	0	1	1	0
2	1	1·26	0·231	$0{\cdot}59_6$	$1{\cdot}19_2$	$0{\cdot}83_8$	$11{\cdot}5_5$
3	1	$1{\cdot}31_6$	$0{\cdot}274_7$	0·77	$1{\cdot}15_5$	$0{\cdot}86_5$	$13{\cdot}7_3$
5	1	$1{\cdot}30_8$	$0{\cdot}268_2$	$0{\cdot}82_2$	$1{\cdot}02_5$	$0{\cdot}97_5$	13·4
6	1	$1{\cdot}29_2$	0·256	$0{\cdot}81_2$	$0{\cdot}97_5$	$1{\cdot}02_5$	12·8
2	2	2	0	0	2	0·5	0
3	2	$2{\cdot}35_2$	$0{\cdot}081_1$	$0{\cdot}38_4$	$2{\cdot}30_1$	0·434	$4{\cdot}0_6$
5	2	$2{\cdot}59_8$	0·131	$0{\cdot}70_9$	2·36	0·424	$6{\cdot}5_5$
1	$\frac{1}{6}$	$0{\cdot}215_3$	$1{\cdot}535_8$	$0{\cdot}81_2$	$0{\cdot}162_5$	6·16	$76{\cdot}7_9$

Interchange of the values of α and β in any case alters the sign of $X_{\text{infl.}}$, g, and of $E_e - E_{\text{infl.}}$, but makes no other difference. It is noticeable that $\left(\frac{dX}{dU}\right)$ min., or $h \underset{\beta\alpha}{\cosh} g$, always approximates in value to the smaller of the two electrode-valencies.

Section 5. *General Application of Method* I.

Equation (2) has two limiting forms,

$$X = \tfrac{1}{2}e^{\alpha U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

$$-X = \tfrac{1}{2}e^{-\beta U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

valid respectively for large positive and large negative values of U. One or other of these will be accurate to 1% as regards X, unless U lies between the limits $\pm (\log 100)/(\alpha + \beta)$; and the region defined by these limits, some $230/(\alpha + \beta)$ millivolts in extent, within which the incompleteness of the analytical reaction exceeds 1%, may be referred to as the "equivalence region." *Outside* this region Method I is applicable and the result of the titration can be determined from a single change of the potential E, without knowledge of E_e, $\overline{E}_0$, G, or H, as follows.

Fully written, equation (29) is equivalent to

$$E = E_0 + \frac{RT}{\alpha F}\log\frac{nM}{V}\gamma_A\theta_A - \frac{RT}{\alpha F}\Sigma\frac{p}{a}\log C_P\gamma_P . \quad . \quad (31)$$

which is therefore valid at all points or stages outside and *before* the equivalence region. Consider two such points, (E, M) and (E', M'), separated by ε millivolts and m c.c. of reagent solution (compare Part I, Section 4). Suppose that at the earlier stage, (E', M'), the amount of the (typical) subsidiary substance P in the titrated solution is nM_P mg.-equivs. [all equivalents being reckoned according to the chemical equation (12)], then if the volume of the solution is V' c.c.,

$$E' = E_0 + \frac{RT}{\alpha F}\log\frac{nM'}{V'}\gamma_A\theta_A - \frac{RT}{\alpha F}\Sigma\frac{p}{a}\log\frac{nM_P}{V'}\gamma_P . \quad . \quad (32)$$

Now, on the addition of m c.c. of the reagent solution, not only is the amount of the titrated substance diminished to nM mg.-equivs., but the volume of the solution is increased to V c.c., and also the amount of the subsidiary substance, P, is either increased or decreased by mn mg.-equivs., according as this substance is, on the whole, a product or a reactant in the analytical reaction (*i.e.*, not merely according as p is positive or negative).

At the later stage, therefore, assuming for the present (see Part I, Sections 2 and 7) that change in the adsorption and activity coefficients can be neglected,

$$E = E_0 + \frac{RT}{\alpha F}\log\frac{nM}{V}\gamma_A\theta_A - \frac{RT}{\alpha F}\Sigma\frac{p}{a}\log n\frac{M_P \pm m}{V}\gamma_P \quad . \quad (33)$$

where $E = (E' - \varepsilon)$, $M = (M' - m)$, and $V = (V' + m)$. Then, by subtraction,

$$\varepsilon = \varepsilon_m + \varepsilon_v\left(1 - \Sigma\frac{p}{a}\right) + \Sigma\frac{p}{a}\varepsilon_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

where

$$\alpha\varepsilon_m = RT/F \,.\, \log(1 + m/M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

$$\alpha\varepsilon_v = RT/F \,.\, \log(1 + m/V') = -RT/F \,.\, \log(1 - m/V) \quad . \quad (36)$$

$$\alpha\varepsilon_P = RT/F \,.\, \log(1 \pm m/M_P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

The effect of the change in the amount of A is represented by ε_m, while the effects of the simultaneous changes in the " subsidiary conditions " (the volume of the solution and the amounts of the subsidiary substances) are represented by the remaining terms on the right of equation (34). In this sense ε_m is the value of the measured potential change "corrected to constant subsidiary conditions," and the correction terms, ε_v, ε_P, etc., are to be found from the tables provided in Part I (*loc. cit.*). It is obvious that, as indicated in Part I, changes in the adsorption and activity coefficients (if not negligible, as assumed) could be corrected for in an entirely similar manner. The result of the titration then follows from the relation

$$M = m \, . \, f(\alpha\varepsilon_m) \, . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

[see Part I, Table I and equations (22) and (26)].

In Part I, the use of the dilution term ε_v is fully demonstrated, a convenient procedure being indicated in Section 12, and a type of case being discussed in Section 8, in which this correction is eliminated owing to the fact that $\Sigma p/a$ is equal to unity. The latter section includes an example of a correction of the ε_P type, P being a product of the reaction (ferric or titanic ion). In this case, on the assumption that P is absent at the commencement of the titration, M_P is accurately known, being simply the number of c.c. of reagent solution already added before the further addition of the m c.c.

On the other hand, in many cases P will be a substance present in considerable excess, M_P will be large in comparison with m, and therefore only a rough estimate (if any) of its magnitude will be required in order to determine the very small correction, ε_P. An example of this would be hydrogen ion as a subsidiary substance in most oxidation–reduction titrations. In short, it is plain that in any particular case, under suitable conditions, the correction of the measured potential changes will readily be reduced to a simple routine.

One special advantage of Method I is that it makes use of less than one half or side of the titration curve, being independent of the equivalence region as well as of all that part of the curve beyond it. This is notably useful in the titration of mixed solutions (*e.g.*, a mixture of halides), where the curves corresponding to the successive reactions overlap and truncate one another. Nevertheless, if the second half of the curve happens to be available, it may be utilised in essentially the same way, the full form of equation (30), valid here, being

$$-E = -E_0' + \frac{RT}{\beta F}\log\frac{-nM}{V}\gamma_B\theta_B - \frac{RT}{\beta F}\Sigma\frac{q}{b}\log C_Q\gamma_Q \quad . \quad (39)$$

If (E, M) and (E'', M'') are the two successive stages, both beyond the equivalence region, and separated by ε' millivolts and m' c.c.

of reagent solution, so that $E'' = (E - \varepsilon')$, $M'' = (M - m')$, and M is negative, we find

$$\varepsilon' = \varepsilon'_m - \varepsilon'_v\,(1 - \Sigma q/b) \quad . \quad . \quad . \quad . \quad . \qquad (40)$$

where

$$\beta\varepsilon'_v = RT/F\,.\log\,(1 + m'/V) \quad . \quad . \quad . \quad . \qquad (41)$$

$$\beta\varepsilon'_m = RT/F\,.\log\left(1 + \frac{m'}{-M}\right) \quad . \quad . \quad . \quad . \qquad (42)$$

and therefore

$$-M = m'\,.f(\beta\varepsilon'_m) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (43)$$

No correction term of the ε_P (or ε_Q) type occurs here, because the chemical reaction has ceased and the *quantities* of the subsidiary substances are not changing.

It has been assumed, so far, that B is the only significant substance (apart from the solvent) introduced by means of the reagent solution. If, however, the latter contains also appreciable quantities of any of the subsidiary substances, or of compounds capable of reacting with the latter (for examples, see Section 11), this merely involves obvious modifications in the form of the subsidiary-conditions correction, for it remains true, in general, that the changes in these conditions are proportional to the quantities of reagent solution added.

In using Method I, should the stage (E, M) be allowed to fall within the equivalence region, the result of the titration will be too high if obtained from the first half of the curve, and too low if from the second half. If $M_{\text{app.}}$ is the erroneous value of M so found, the error in the former case is approximately $(H/2)^{1+\beta/\alpha}/M_{\text{app.}}^{\beta/\alpha}$, and the same with α and β interchanged in the latter case. In either case, an alternative formulation of the error is $M_{\text{app.}}\,.f[(\alpha + \beta)(E \sim E_e)]$.

Thus, approximate knowledge of *either* H or E_e would permit the correction of this error if not too large. Such procedure, of course, would really constitute a crude form of Method II.

Section 6. *General Forms of Methods* II *and* III.

Apart from its special advantages, the absolute precision of Method I is higher than that attainable under the most favourable conditions by the customary potentiometric methods. Sometimes, however (as when dealing with unusually dilute solutions or with an analytical reaction of low inherent sensitivity), it may be desirable to seek the appreciable increase of precision which is, in general, to be obtained by making use of a stage nearer to the point of inflexion than is permissible in Method I. Of the two distinct methods of so doing, Method II makes use of only one half or side of the titration curve, but requires some knowledge of the unit H, whereas Method III requires no knowledge of H but utilises both halves of the curve. Properly applied, either method yields the highest absolute precision obtainable with a given experimental system. Potentiometric methods of the "absolute" type (see introductory remarks in Part I) should theoretically yield the same maximal precision, but in practice this is not realised because the absolute values of the measured potential are not nearly so accurately reproducible as are the differences or changes on which alone the differential methods depend.

Method II.—Consider, as in the last section, two successive stages (E', M') and (E, M), separated by ε millivolts and m c.c. of reagent solution; but suppose, now, that the second stage lies within the equivalence region, so that the limiting form (31) is not valid at this stage. Applying, instead, the general equation, we may write

$$M/H = \underset{\alpha\beta}{\sinh} U \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where U is defined by equation (23).

At the earlier stage the measured potential has the value E', or $(E + \varepsilon)$, but this is, in effect, "corrected" to a value $(E + \varepsilon_m)$, in the manner to be explained in the following section, whereupon both H and G may be treated as constants; hence, using the same value of H as in (44),

$$(M + m)/H = \underset{\alpha\beta}{\sinh} (U + u) \quad . \quad . \quad . \quad . \quad (45)$$

where

$$u = F/RT \, . \, \varepsilon_m \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Now the following identity can easily be verified,

$$\underset{\alpha\beta}{\sinh} (U + u) - \underset{\alpha\beta}{\sinh} U = \underset{\alpha\beta}{\sinh} u \, . \, \underset{\alpha\beta}{\cosh} (U + \phi) \, . \, \underset{\alpha\beta}{\operatorname{sech}} \phi \quad . \quad (47)$$

where

$$(\alpha + \beta)\phi = \log \frac{1 + f(\beta\varepsilon_m)}{f(\alpha\varepsilon_m)} \quad . \quad . \quad . \quad . \quad . \quad (48)$$

or, for large values of ε_m,

$$(\alpha + \beta)\phi \approx \alpha u + f(\beta\varepsilon_m) - f(\alpha\varepsilon_m) \quad . \quad . \quad . \quad (49)$$

$$\approx \alpha u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

Thus, if equation (48) is written in the form

$$\underset{\alpha\beta}{\operatorname{sech}} (U + \phi) = (H/m) \underset{\alpha\beta}{\sinh} u \, . \, \underset{\alpha\beta}{\operatorname{sech}} \phi \quad . \quad . \quad (51)$$

and coupled with equation (44), it is apparent that when m and ε have been measured and H is known, M may be obtained by the use of a parallel table of the functions $\underset{\alpha\beta}{\sinh}$ and $\underset{\alpha\beta}{\operatorname{sech}}$ in a manner essentially similar to that described in Part II (pp. 862, 863). The corresponding curves shown in Figs. 1 and 2 would be a (less accurate) substitute for such tables since there is no objection to dividing both sides of equation (51) by h. Alternatively, of course, suitable diagrams, after the manner of those shown in Part II (Figs. 1 and 2), could be constructed.

Method III.—Introducing a third and later stage (E'', M'') *beyond* the equivalence region and separated from the second stage by ε' millivolts and m' c.c. of reagent solution, and supposing as before that the correction of Section 7 is applied, the measured potential $(E - \varepsilon')$ being corrected to $(E - \varepsilon'_m)$, then we have

$$(M - m')/H = \underset{\alpha\beta}{\sinh}\,(U - u') \quad . \quad . \quad . \quad (52)$$

where

$$u' = F/RT \, . \, \varepsilon'_m \quad . \quad . \quad . \quad . \quad (53)$$

Between the three equations (44), (46), and (53), both H and U can be eliminated, and the following exact equation obtained,

$$M = \frac{m \underset{\alpha\beta}{\operatorname{cosech}} u - m' \underset{\beta\alpha}{\operatorname{cosech}} u'}{\underset{\alpha\beta}{\coth} u + \underset{\alpha\beta}{\coth} u' - \underset{\alpha\beta}{\operatorname{cosech}} u - \underset{\beta\alpha}{\operatorname{cosech}} u'} \quad . \quad (54)$$

For large values of u and u', such as will in practice be used, equation (54) can be reduced to the much more convenient approximate form

$$M_{\text{app.}} = m \, . \, f(\alpha\varepsilon_m) - m' \, . \, f(\beta\varepsilon'_m) \quad . \quad . \quad . \quad (55)$$

The error involved in this approximation is of the order of magnitude of

$$(m - m' + 2M_{\text{app.}}) \, . \, f(\alpha\varepsilon_m + \beta\varepsilon'_m) \quad . \quad . \quad . \quad (56)$$

and so is negligible when ε_m and ε'_m are both large.

Equations (29) and (30) of Part II are complicated by the terms involving V which there represent (approximate) allowance for volume change, but on omitting these terms and (in compensation) altering ε and ε' to ε_m and ε'_m, we see that these equations represent the special case where $\alpha = \beta = 1$ (see examples in Section 7).

Section 7. *Correction for Variation in* H *and* G.

It is essential to the increased precision of Methods II and III, as compared with Method I, that the stage (E, M) should lie within the equivalence region, so that equation (33), for example, no longer holds good. Nevertheless, the additive corrections (described in Section 5) for change in the subsidiary conditions are still essentially valid, being equivalent in effect to making H and G constant, *with the values they attain at the stage* (E, M). For, consider again the stage (E', M') which is outside and *before* the equivalence region, so that equation (32) still applies. If, now, without altering the amount (nM mg.-equivs.) of the titrated substance, we could alter the subsidiary conditions, the volume from V' to V, and the amount of the subsidiary substance P from nM_P to $n(M_P \pm m)$ mg.-equivs., etc., it is obvious that E' would be altered to

$$E'(\text{corr.}) = E' - \varepsilon_v\left(1 - \Sigma\frac{p}{a}\right) - \Sigma\frac{p}{a}\varepsilon_P \quad . \quad . \quad (57)$$

where ε_v and ε_P are defined by equations (36) and (37). Now, at the stage (E, M) the subsidiary conditions *actually* are V, and, to a close approximation, $n(M_P \pm m)$, etc., the error of the latter approximation (due to the incompleteness of the analytical reaction) being only $\frac{1}{2}nHe^{-\beta V}$, which may be neglected in comparison with nM_P. In other words, E' (corr.) is the value the potential would possess at the stage (E', M') *if the subsidiary conditions (and therefore* H *and* G) *had those values which they actually attain at the stage* (E, M).

Since $E' = (E + \varepsilon)$, we may write

$$E'(\text{corr.}) = (E + \varepsilon_m) \quad . \quad . \quad . \quad . \quad . \quad (58)$$

where ε_m is defined by equation (34). In an exactly similar manner, it can be shown that if ε'_m is defined by equations (40) and (41), the value which the potential would possess at the stage (E'', M'') (which is *beyond* the equivalence region), if H and G still had those values which they actually attained at the stage (E, M), is

$$E''(\text{corr.}) = (E - \varepsilon'_m) \quad . \quad . \quad . \quad . \quad . \quad (59)$$

In applying these corrections, it is usually convenient to adopt the procedure indicated in Part I, Section 12, correcting the measured potentials to some simple round value of each subsidiary condition. It is true that such correction is artificial as applied to the stage (E, M) because the latter is in the equivalence region, and the corrected value of E will not be the value it would attain if the subsidiary conditions were altered to the stated round values. Nevertheless, if E is corrected in the same manner as E', the difference between these corrected values will be ε_m, as defined above. And similarly, if E is corrected in the same manner as E'', *i.e.*, as if it were *beyond* the equivalence region, then the difference between the corrected E and E'' will be ε'_m as defined above.

For example, take the simple case of the chloride titrations recorded in Part II (p. 868). As explained there, the *E.M.F.* of the silver chloride–quinhydrone cell used is doubly affected by dilution when the chloride is in marked excess, and is unaffected by dilution when the silver ion is in excess. In this case, therefore, equations (34) and (40) assume the special forms

$$\varepsilon_m = \varepsilon - (2RT/F) \,.\, \log V/V'$$
$$\varepsilon'_m = \varepsilon'$$

Now if E' is corrected to some convenient volume, such as 100 c.c., it becomes (say) E'_a by addition of a correction of the first form,

$$\text{Corr. }(a) = (2RT/F) \,.\, \log V'/100 \quad . \quad . \quad . \quad . \quad . \quad (60)$$

$$E'_a = E' + (2RT/F) \,.\, \log V'/100 \quad . \quad . \quad . \quad (61)$$

and if E is " corrected " in the same manner,

$$E_a = E + (2RT/F) \,.\, \log V/100$$

then, by subtraction,

$$E'_a - E_a = \varepsilon - (2RT/F) \,.\, \log V/V' = \varepsilon_m.$$

On the other hand, E'' is corrected to any convenient volume by the addition of a different form of correction, which in this particular case is zero,

$$\text{Corr. }(b) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

$$E''_b = E'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

and, of course, on " correcting " E in the same way and subtracting,

$$E_b - E''_b = \varepsilon' = \varepsilon'_m.$$

For the sake of comparison, two of the titrations recorded in Part II (Examples 1 and 2, p. 868) are worked out below according to the newer and generally applicable procedure, which will be seen to be also much simpler arithmetically. In order to make the examples more generally illustrative, the second form of correction [Corr. (*b*)] is explicitly stated and applied, although in this special case it happens to be zero throughout.

Example 1. 1000 C.c. of $N/1000$-KCl titrated by $N/100$-$AgNO_3$ (actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/2000$); temp. ≈ 14·5°.

The application of Method III begins at Stage II, when 85 c.c. of silver nitrate have already been added in applying Method I. The latter method having shown that between 13 and 14 c.c. are still required to reach equivalence, two successive additions of 13 c.c. and 12 c.c. respectively are made, and the potentials at Stages III and IV measured. The three measured potentials are corrected to 17°, and then the first and second are corrected to 1000 c.c. volume in the manner (*a*) [see equations (60) and (61)], and the second and third to any convenient volume in the manner (*b*) [see equations (62) and (63)], and ε_m and ε'_m are obtained by subtraction.

Stage.	$\frac{V}{1000}$.	Corr. (*a*).	Corr. (*b*).	E (expt.).	$E_{17°}$.	E_a.	E_b.
II	1·085	$4{\cdot}0_5$		172·2	$173{\cdot}6_5$	177·7	
III	1·098	$4{\cdot}6_5$	0	118·1	119·1	$123{\cdot}7_5$	119·1
IV			0	58·3	58·8		58·8
					By subtraction	$53{\cdot}9_5$	60·3

Then, to find M at Stage III, and hence M_0 :

$m = 13 \qquad \epsilon_m = 53{\cdot}9_5 \qquad f(\epsilon_m) = 0{\cdot}130_2 \qquad m\,.\,f(\epsilon_m) = 1{\cdot}69_3$

$m' = 12 \qquad \epsilon'_m = 60{\cdot}3 \qquad f(\epsilon'_m) = 0{\cdot}098_5 \qquad m'\,.\,f(\epsilon'_m) = 1{\cdot}18_2$

By subtraction, $M = 0{\cdot}51$

and by addition of 98·0, $M_0 = 98{\cdot}51$

Example 2. 100 C.c. of $N/1000$-KCl titrated by $N/1000$-$AgNO_3$ (actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/4000$); temp. $\sim$ 20°.

The procedure is essentially as in Example 1, except that two stages (III and IV) within the equivalence region are used, in turn, as the stage (E, M), so that two results are obtained which are then averaged.

For the purpose of the dilution correction, 100 c.c. is taken as a convenient round value of the volume.

Stage.	$\frac{V}{100}$.	Corr. (*a*).	Corr. (*b*).	E (expt.).	$E_{17°}$.	E_a.	E_b.
II	1·75	28·0		190·4	188·5	216·5	
III	1·96	$33{\cdot}6_5$	0	139·8	138·4	$172{\cdot}0_5$	138·4
IV	2·00	$34{\cdot}6_5$	0	120·5	119·3	$153{\cdot}9_5$	119·3
V			0	68·4	67·7		67·7
					By subtraction	$44{\cdot}4_5$	70·7
						$62{\cdot}5_5$	51·6

(i) To find M at Stage III, and hence M_0 :

$m = 21 \qquad \epsilon_m = 44{\cdot}4_5 \qquad f(\epsilon_m) = 0{\cdot}2034 \qquad m\,.\,f(\epsilon_m) = 4{\cdot}27_1$

$m' = 29 \qquad \epsilon'_m = 70{\cdot}7 \qquad f(\epsilon'_m) = 0{\cdot}0629 \qquad m'\,.\,f(\epsilon'_m) = 1{\cdot}82_4$

By subtraction, $M = 2{\cdot}45$

By adding 96·0, $M_0 = 98{\cdot}45$

(ii) To find M at Stage IV, and hence M_0 :

$m = 25 \qquad \epsilon_m = 62{\cdot}5_5 \qquad f(\epsilon_m) = 0{\cdot}0892_6 \qquad m\,.\,f(\epsilon_m) = 2{\cdot}23_1$

$m' = 25 \qquad \epsilon'_m = 51{\cdot}6 \qquad f(\epsilon'_m) = 0{\cdot}1454 \qquad m'\,.\,f(\epsilon'_m) = 3{\cdot}63_5$

By subtraction, $M = -1{\cdot}40$

By adding 100·0, $M_0 = 98{\cdot}60$

Average of two results in Example 2, $M_0 = 98{\cdot}52_5$.

In Example 2, the values of Corr. (a) are seen to be large, but this does not mean that it will be liable to introduce appreciable errors into the result of the titration, or that the subsidiary condition V needs to be very accurately known, for it is only the *change* in Corr. (a)—amounting to 6·65 millivolts in all—which affects the corrected difference ε_m.

Section 8. *Complete Temperature Correction.*

If, as in the above examples, the measured potentials are multiplied by $(290/T)$, this has the effect of multiplying the differences ε and ε' by the same factor, which makes allowance for the fact that the unit (RT/F) is proportional to the absolute temperature.

This is all that is required so long as the temperature does not vary much during a titration.

In working at temperatures other than "room temperature," however, considerable fluctuations are not easily avoided under practical conditions for titration. Even if a thermostat is used it is very troublesome to keep the reagent at the same temperature, while, if it is not so kept, time is lost after each addition in waiting for temperature equilibrium. It is therefore quicker and simpler to make no attempt to maintain a fixed temperature, but to read the thermometer at each stage and apply a complete temperature correction in the following manner.

For such variation as will occur during a titration both E_0 and E'_0 may be assumed to depend linearly on the temperature. This means that if the temperature coefficient of the potential E is measured at *any* stage outside the equivalence region, the quantity $(E - T \, . \, dE/dT)$ will be found to possess one or other of two values, say E_{00} and E'_{00}—the former at any stage *before* the equivalence region, the latter at any *beyond* it. Two such measurements will therefore suffice to determine these two constants, which are all that we require for the purpose of the complete temperature correction.

If T', T, and T'' are the temperatures of the system at the successive stages (E', M'), (E, M), and (E'', M'') in Method III, it is easily shown that when the potential changes, ε and ε', are corrected for the *variation* of temperature during titration, as well as for the value of the unit, RT/F, they become

$$\varepsilon_{17^\circ} = 290(E' - E_{00})/T' - 290(E - E_{00})/T \quad . \quad . \quad (64)$$

$$\varepsilon'_{17^\circ} = 290(E - E'_{00})/T - 290(E'' - E'_{00})/T'' \quad . \quad (65)$$

so that for differential purposes $290(E' - E_{00})/T'$ and $290(E'' - E'_{00})/T''$ may be used as temperature-corrected values of E' and E'' respectively, while E has two such values—one $290(E - E_{00})/T$, as if it were *before* the equivalence region, and the other $290(E - E'_{00})/T$, as if it were *beyond* that region. There is here an obvious analogy in principle with the procedure discussed in the latter part of Section 7. If ε_{17° is re-written in the form

$$\varepsilon_{17^\circ} = \frac{290}{T}\left[\left\{\frac{T}{T'}(E' - E_{00}) + E_{00}\right\} - E\right] \quad . \quad . \quad (66)$$

its derivation will be obvious, and it will be seen that the accuracy of the correction depends on the assumption that $(E' - E_{00})$ is proportional to the absolute temperature over some range including T and T' *but not necessarily including* 290° Abs. That it does not depend on accurate knowledge of E_{00} will be seen if ε_{17° is again re-written as

$$\varepsilon_{17^\circ} = \frac{290}{T'}E' - \frac{290}{T}E + \left(\frac{290}{T} - \frac{290}{T'}\right)E_{00} \quad . \quad . \quad (67)$$

since the coefficient of E_{00} is small. Similar considerations apply to ε'_{17°.

Section 9. *Precision of the Generalised Method.*

Writing U' for $(U + u)$, and using the abbreviations Δ sech and Δ tanh for the positive differences $[\underset{\alpha\beta}{\operatorname{sech}}\,(U + g) - \underset{\alpha\beta}{\operatorname{sech}}\,(U' + g)]$ and $[\underset{\alpha\beta}{\tanh}\,(U' + g) - \underset{\alpha\beta}{\tanh}\,(U + g)]$ respectively, we may formulate the error dM of a titration by Method II as follows :

$$- dM = \frac{Hh}{\Delta\,\operatorname{sech}}du + \frac{\Delta\,\tanh}{\Delta\,\operatorname{sech}}(\underset{\beta\alpha}{\cosh}\,g)dH \quad . \quad . \quad (68)$$

where du and dH represent (small) errors in u and H. Under the conditions of highest sensitivity, when $U \approx - 2\,g$ and u is large, this reduces to

$$- \frac{dM}{h\,.\,\underset{\beta\alpha}{\cosh}\,g} \approx H\,.\,du + \frac{dH}{\beta} \quad . \quad . \quad . \quad . \quad (69)$$

and it has been seen (Section 4) that $h\,.\,\underset{\beta\alpha}{\cosh}\,g$ is approximately equal to the smaller of the two electrode-valencies.

Similarly, writing U'' for $(U - u')$, and Δ' sech and Δ' tanh for the analogous positive differences, due regard being paid to the fact that u and u' have opposite signs, we derive the following equation for the error of a titration by Method III :

$$\frac{dM}{Hh}\left[\frac{\Delta\,\operatorname{sech}}{\Delta\,\tanh} + \frac{\Delta'\,\operatorname{sech}}{\Delta'\,\tanh}\right] = \frac{du'}{\Delta'\,\tanh} - \frac{du}{\Delta\,\tanh} \quad . \quad . \quad (70)$$

which is the generalised form of equation (37) of Part II.

Under optimum conditions, when $U \approx - 2\,g$ and both u and u' are large, equation (70) reduces to

$$\frac{dM}{Hh\,\underset{\beta\alpha}{\cosh}\,g} \approx \frac{\alpha du' - \beta du}{\alpha + \beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

showing that (under these conditions) equal *and opposite* errors in u and u' will have the same effect as a single error of the same magnitude as either in u in Method II. The precision of Method II, however, depends also on the correctness of the value assigned to H. Thus from equation (69), $- \partial M/\partial H$ would be approximately equal to either unity or α/β according as α is greater or less than β, *i.e.*, it would not be greater than unity and might be much less.

Of course, Method II, like Method I, can be applied to the second half of the curve if this is available. For this case equation (68) would be modified in an obvious manner, and instead of equation (69) we should have

$$\frac{dM}{\underset{\beta a}{h \cosh g}} \approx H \,.\, du' + \frac{dH}{\alpha} \quad . \quad . \quad . \quad . \quad . \qquad (72)$$

showing that the maximal sensitivity is the same, but $\partial M/\partial H$ is now (approximately) equal to either unity or β/α.

Section 10. *An Alternative Geometrical Form of Method* I.

The Straight-line Method.—If, as in Section 7, E_a represents the value of the measured potential when " corrected " in the manner proper to any stage before the equivalence region, then equation (31) is equivalent to $E_a = \text{constant} + RT/\alpha F \,.\, \log M$. The (unknown) constant may be written in the form $- RT/\alpha F \,.\, \log k$, and E_a in the substituted form $RT/\alpha F \,.\, \log y$, whereupon the equation reduces to $ky = M = M_0 - (M_0 - M)$, where y is equal to $e^{(\alpha F/RT)E_a}$.

If, then, the corrected potential at each stage is plotted on a suitable *exponential scale*, against the number of c.c. of reagent present, the successive points *will lie on a straight line*, which cuts the axis at a point indicating the result of the titration. Thus two points or stages suffice to determine the result (the more accurately if they are well separated), but also, owing to the exponential scale, it will be found that the determination becomes very much more certain as the final measurement more nearly approaches the equivalence point, provided always that it do not fall within the equivalence region. All this corresponds exactly with the conditions of precision in the ordinary or algebraic form of the method.

The geometrical form, however, provides a useful general method for investigating new or uncertain systems, since if a number of points are plotted (instead of merely two) their adherence to a straight line is a strong indication, amounting almost to conclusive proof, that equilibrium conditions are being realised.

A suitably graduated scale is easily constructed. The distances being proportional to e^x, the graduations are placed at convenient intervals of $(RT/\alpha F)x$ [or, for 17°, $(25/\alpha)x$] and numbered consecutively in millivolts, *commencing with any convenient number.* The test and the certainty of the result can be improved if the second half of the titration curve is available, for, corresponding to this, a second straight line should be obtainable, passing through the same end-point, the equation being $k'y' = (M_0 - M) - M_0$, where $y' = e^{-(\beta F/RT)E_b}$.

Section 11. *Importance of the Symmetrical Case.*

Application in Acidimetry and Alkalimetry.—It will be noticed that, *even in the symmetrical case* where $\alpha = \beta$, the titration-curve equation and the methods dependent on it are now much more general in application than those obtained in Part II, since the latter took no account of subsidiary reactants and products. For example, with the new equation, and the general form of subsidiary-conditions correction described in Section 7, the following important cases can be dealt with in a simple manner.

Case (1). In the titration of a *weak base* (such as ammonia) against a strong acid, the former being the added substance, the equation for the analytical reaction is properly written

$$H^{\bullet} + NH_3 = NH_4^{\bullet} \quad . \quad . \quad . \quad . \quad . \quad (73)$$

(K being *ca.* 5×10^{-10}, *i.e.*, $10^{-14}/2 \times 10^{-5}$ or K_w/K_b) and if a hydrogen electrode or its equivalent is used as indicator electrode, the alternative electrode reactions are

$$\left.\begin{aligned} \ominus + H^{\bullet} &= \tfrac{1}{2}H_2 \\ -\ominus + NH_3 &= NH_4^{\bullet} - \tfrac{1}{2}H_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (74)$$

The principal reactants are, in effect, hydrogen ion and the base, the amount of hydroxyl ion present being relatively quite negligible until far beyond the equivalence region, unless excessively dilute solutions are being used.

Case (2). Exactly the same equations are applicable to the titration of a *strong* base against a strong acid *in the presence of an appreciable amount of a salt of a weak base*, for in that case, owing to the weakness of the base, the addition of hydroxyl ions (*i.e.*, the strong base) is exactly the same in effect as adding an equivalent quantity of the *weak* base and, at the same time, withdrawing an equivalent quantity of the positive ion of its salt, thus

$$OH' = NH_3 + H_2O - NH_4^{\bullet} \quad . \quad . \quad . \quad . \quad (75)$$

The additional molecule of water makes no difference, while the withdrawal of the positive ion only affects the form of the subsidiary-conditions correction.

Case (3). The titration of a *salt of a weak acid* against a strong acid is really entirely analogous to Case (1), the negative ion of the salt behaving essentially like the weak base. For example, with borax (which in solution is essentially NaH_2BO_3 mixed with an equimolar quantity of free boric acid) the analytical reaction is

$$H^{\bullet} + H_2BO_3' = H_3BO_3 \quad . \quad . \quad . \quad . \quad . \quad (76)$$

(K being *ca.* 10^{-9}) and the electrode reactions are

$$\left.\begin{aligned} \ominus + H^{\bullet} &= \tfrac{1}{2}H_2 \\ -\ominus + H_2BO_3' &= H_3BO_3 - \tfrac{1}{2}H_2 \end{aligned}\right\} \quad . \quad . \quad . \quad (77)$$

The principal reactants are hydrogen ion and the dihydrogen-borate ion, and it is only an incidental matter affecting the form of the subsidiary-conditions correction that, in this particular case, an equivalent amount of free boric acid accompanies the added substance.

Case 4. From the same analogy, it follows that the equations of Case (3) are applicable to the titration of a strong base against a strong acid *in the presence of an appreciable amount of a weak acid.* The addition of the hydroxyl ion is exactly the same in effect as adding an equivalent quantity of the negative ion of the weak acid, and at the same time withdrawing an equivalent quantity of the weak acid itself :

$$OH' = H_2BO_3' + H_2O - H_3BO_3 \quad . \quad . \quad . \quad (78)$$

and the latter withdrawal merely modifies the subsidiary-conditions correction.

Finally, four cases analogous to the above are obtained on interchanging the words " acid " and " base," making obvious equivalent alterations with regard to the ions, and adopting as indicator electrode either the hydrogen electrode or any other which behaves *in alkaline solution* as a " hydroxyl electrode." Treated in this manner, the eight cases are seen to be essentially one and the same, and the equations of this section, taken in conjunction with the preceding general theory, show how these common titrations of acidimetry and alkalimetry may be made to yield the highest possible precision.

Summary.

It is shown that both the titration-curve equation and the new methods of titration given in two previous papers can be fully generalised, *i.e.*, made applicable to a system involving both analytical and electrode reactions of the most general type.

The characteristic forms of the curves represented by the generalised equation, and of the derived curves, are indicated with the aid of diagrams, and some concrete examples cited. The more important mathematical properties of the curves are exhibited, the generalised methods of titration deduced, and their precision formulated, in terms of certain bin-exponential functions, regarded as generalised hyperbolic functions. Methods I and III, however, still involve only the single function, *f*, tabulated in the first of this series of papers.

A routine procedure previously indicated is now more fully developed, whereby, in connexion with all three methods, accurate allowance is made for unavoidable variations in the subsidiary conditions, *i.e.*, the volume of the solution and the concentrations

of subsidiary reactants and products. A simple mode of correction is also provided for any unavoidable *fluctuations* of temperature.

In Section 10, a *geometrical* form of Method I is outlined (a " straight-line method "), suitable for the investigation of new and uncertain systems, since it provides a stringent test as to the attainment of equilibrium in the system.

Finally, the advantage of the more general form of the titration-curve equation, even in the symmetrical case, is pointed out and exemplified by its application to the titrations of acidimetry and alkalimetry involving weak acids, weak bases, and their salts.

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