Oxidation-Reduction Titration Curve

Both Half Reactions Homogeneous in Coefficient

by

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요 약

균일계수 산화환원 적정에 있어서의 전위의 적정분율에 따른 변화를 나타내는 정확한 방정식을 얻었다. 이 방정식은 적정곡선이 시약의 농도에 무관계함을 알려준다. 또한 전위차적정범위 종말점의 예민도는 반전지의 기준전위의 차는 물론, 각 반반응에 관여하는 전자수에 따라 심한 영향을 받음을 알려준다. 적정곡선의 변곡점이 당량점과 일치하지 않음을 증명하였다. 또한 적정단계에 따른 반응의 완결도를 평형상수식을 토대로 하여 해석하였다. 이 결과는 산화환원 이외의 평형에도 적용된다.

Abstract

An exact expression of the titration fraction as a function of the potential is derived for the cases where the coefficients of the both half reactions involved in the titration are homogeneous. It shows that the potential is independent of the concentration of the reagents not only at the equivalence point but also at all titration fractions. The sharpness of the end point detection by potentiometric method is shown to depend not only on the difference of the normal potentials involved but also strongly on the number of electrons transferred in each half reaction. The inflexion point of the potentiometric titration curve is shown to be slightly off from the equivalence point, including the cases where the number of electrons involved are equal. Completeness of the reaction in the course of titration is analyzed, too, mostly in terms of equilibrium constant, thus most of the results are applicable to any type of equilibrium in a single phase with particular relatiohnsip of coefficients of chemical equation.

Introduction

It has been shown that the equivalence-point potential of the oxidation-reduction titration is independent of the concentration of the reagents only when the half reactions involved are homogeneous in coefficie-

nt[1,2]. Recently, a scheme of the numerical computations of the titration curve has been developed[2,3].

The present work is concerned with derivation of an exact equation of potentiometric titration curve and the analysis of the quantitativeness of titration reaction for the cases where only the homogeneous half rea-

tion equations are involved. Furhtermore, some practical situations are analyzed on the basis of the derived results.

Titration Curve Equation

Let the reductant titrand system, of formal potential E^0_1, be represented by Eq. (1), and the oxidant titrant system, of formal potential E^0_2, be represented by Eq. (2):

$$Ox_1 + n_1e \leftrightarrows Red_1; \qquad E^0_1 \qquad (1)$$

$$Ox_2 + n_2e \leftrightarrows Red_2; \qquad E^0_2 \qquad (2)$$

When V_0 ml of C_0 molar solution of Red_1 is titrated with C molar solution of Ox_2 up to V ml addition, the equilibrium concentrations of the chemical species involved in the titration reaction are given by

$$[Red_1] = C_0V_0(1-\alpha)/(V+V_0) \qquad (3)$$

$$[Ox_1] = C_0V_0\alpha/(V+V_0) \qquad (4)$$

$$[Red_2] = \frac{C_0V_0\alpha}{V+V_0} \cdot \frac{x}{y} \qquad (5)$$

$$[Ox_2] = \frac{CV-(x/y)C_0V_0\alpha}{V+V_0} \qquad (6)$$

respectively, where α designates the fraction of Red_1 converted to Ox_1 and x and y are the coefficients in the titration reaction

$$xOx_2 + yRed_1 \rightleftarrows xRed_2 + yOx_1 \qquad (7)$$

Thus $xn_2 = yn_1$ holds.

Since the potential of the two systems will have the same value when the reaction has reached equilibrium, at any selected point in the titration, the Nernst expressions can be written as

$$E = E^0_1 + (1/n_1\varphi)\ln\alpha/(1-\alpha) \qquad (8)$$

$$E = E^0_2 + (1/n_2\varphi)\ln(\phi-\alpha)/\alpha \qquad (9)$$

where ϕ designates the titration fraction

$$\phi = (CVy)/(C_0V_0x) = (CVn_2)/(C_0V_0n_1) \qquad (10)$$

and φ is an abbreviation

$$\varphi = F/RT \qquad (11)$$

Multiplication of Eq. (8) by n_1 and of Eq. (9) by n_2, followed by addition gives a general equation for the potential of the solution at any given titration fraction:

$$E = \frac{n_1E^0_1 + n_2E^0_2}{n_1+n_2} + \frac{1}{n_1+n_2}\frac{1}{\varphi}\ln(\phi-\alpha)/(1-\alpha) \qquad (12)$$

Evidently, at the equivalence point, $\phi=1$, the potential is given by the first term of Eq. (12), and it is independent of the concentration of the reagents. Solving for α, Eq. (8) gives

$$\alpha = \frac{\exp[n_1\varphi(E-E^0_1)]}{1+\exp[n_1\varphi(E-E^0_1)]} \qquad (13)$$

Substitution of Eq. (13) into Eq. (9), followed by solving for ϕ results in

$$\phi = \alpha[1+\exp n_2\varphi(E-E^0_2)] \qquad (14)$$

and

$$\phi = \frac{\exp n_2\varphi(E-E^0_1) + \exp(n_1+n_2)\varphi(E-E_{eq})}{1+\exp n_1\varphi(E-E^0_1)} \qquad (15)$$

respectively, where

$$E_{eq} = \frac{n_1E^0_1 + n_2E^0_2}{n_1+n_2} \qquad (16)$$

Eq. (15) is a titration curve equation, and it shows that the potential is independent of the concentration of the reagents not only at the equivalence point but throughout the titration. The titration error at a given potential can be derived from Eq. (15) as

$$\phi - 1 = \frac{\exp(n_1+n_2)\varphi(E-E_{eq}) - 1}{1+\exp n_1\varphi(E-E^0_1)} \qquad (17)$$

Eq. (17) provides valuable criterion in planning the potentiometric titration up to a preassigned potential, since $\phi-1$ at a given value of E designates the titration error. Changing variable by

$$E = E_{eq} + \epsilon \qquad (18)$$

converts Eq. (17) into a convenient form for practical use:

$$\phi - 1 = \frac{\exp(n_1+n_2)\varphi\epsilon - 1}{1+A\exp n_1\varphi\epsilon} \qquad (19)$$

where

$$A = \exp\frac{n_1n_2}{n_1+n_2}\varphi\Delta E_0, \qquad \Delta E_0 = E^0_2 - E_1 \qquad (20)$$

It is interesting to note that, when $E = E^0_1$, $\epsilon = -n_2\Delta E_0/(n_1+n_2)$,

$$\phi = \frac{1}{2}[1+\exp(-n_2\varphi\Delta E_0)] \qquad (21)$$

and when $E = E^0_2$, $\epsilon = n_1n_2\Delta E_0/(n_1+n_2)$,

$$\phi = 2\left(1 + \frac{1}{1+\exp n_1\varphi\Delta E_0}\right) \qquad (22)$$

Thus, the errors in assuming that $E = E^0_1$ at $\phi = \frac{1}{2}$ and $E = E^0_2$ at $\phi = 2$ are determined by the magnitudes of $n_1\Delta E_0$ and $n_2\Delta E_0$, respectively. It should be remembered that Eqs. (8), (9), and hence (15) and (17) are not applicable, when ϕ is close to zero, because pure solutions of the reagents cannot be obtained due to the redox properties of water. Furthermore, the titration error at a preassigned value of potential is determined by the magnitude A which depends strongly on both ΔE_0 and n_1 and n_2. (see Eq. (20) and Fig. 1).

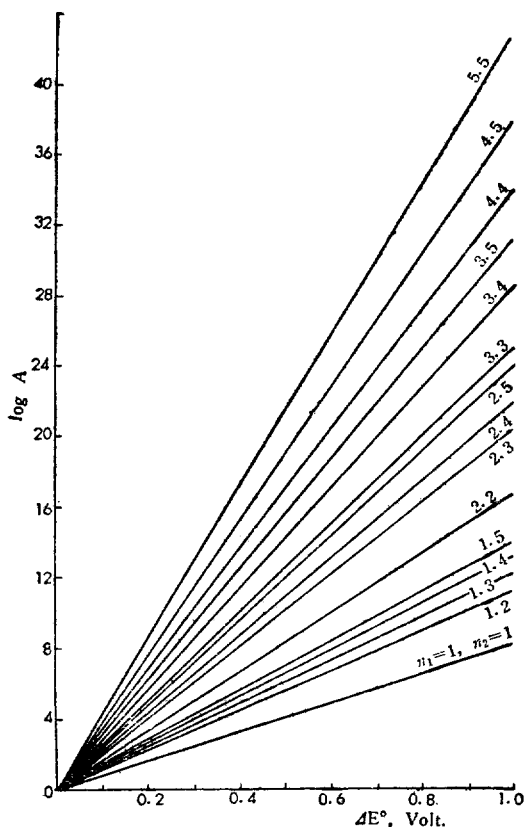Although it is difficult to express the potential as

Figure 1

a function of ϕ in a simple form, Eqs. (15) and (19) can be used in analyzing various features of the titration curve. A family of potential-titration fraction curves can be obtained by calculating ϕ for a set of ε. Fortunately, the curves are independent of the concentration of the reagents involved but dependent only on n_1, n_2 and E_q.

Quantitativeness of Reaction

The quantitativeness of the reaction can be expressed either by

$$\zeta_r = \phi - \alpha \qquad (23)$$

or by

$$\zeta_r' = 1 - \alpha \qquad (24)$$

for the Red_1, and

$$\zeta_0 = \frac{1 - \alpha}{\phi} \qquad (25)$$

for the Ox_2.

In view of the Eqs. (13) and (15), those relative reaction deficiencies can be written as the functions of ε:

$$\zeta_r = \frac{1}{1 + A\exp(-n_2\varphi\varepsilon)} \qquad (26)$$

$$\zeta_r' = \frac{\exp(n_1 + n_2)}{1 + A\exp n_1\varphi\varepsilon} \qquad (27)$$

and

$$\zeta_0 = \frac{1}{1 + A\exp(-n_2\varphi\varepsilon)} \qquad (28)$$

Eq. (28) is particularly useful in determining the required titration fraction to give a perceptible color of the titrant, such as permanganate in the permanganometry, when used in conjunction with Eq. (19). Thus, if A is sufficiently large, which will be the case in practical titrations, Eq. (28) may be approximated by

$$\zeta_0 = \frac{\exp n_2\varphi\varepsilon}{A} \qquad (28')$$

for smaller values of ε; i.e., in the vicinity of the equivalence point. The region where Eq. (28') applies can not be seen in a straightforward way. However, noting that

$$\exp n_2\varphi\varepsilon = A$$
$$\exp n_1\varphi\varepsilon = An_1/n_2 \qquad (29)$$

when $\varepsilon = E_2^*-E_{eq}$, and cosidering the subsequent discussion of the rate of variation of the potential with titration fraction, such region is considered to be confined to the extreme vicinity of the equivalence point. Assuming that the perceptible concentration of Ox_2 is in such region, the titration error in the visual notion of its color can be estimated by rewriting Eq. (19) as

$$\phi - 1 = \frac{A(n_1 + n_2)/n_2(c/c')\ (n_1 + n_2)/n_2 - 1}{1 + A(n_1 + n_2)/n_2(c/c')\ (n_1/n_2)} \qquad (30)$$

where c and c' designate the minimum perceptible concentration of Ox_2 and the concentration of the titrant corrected for the volume factor at the equivalence-point, respectively.

As an illustrative example, the titration errors computed for the titration of ferrous iron with permanganate from Eq. (30) taking $c = 1 \times 10^{-5}$M are $^1/_2 \times 10^{-4}$ and $^1/_2 \times 10^{-3}$ for the concentrations of the permanganate used 0.1N and 0.01N, respectively. The error caused in subtracting the blank value at a given tittation is represented by

$$\phi - \phi\zeta_0 - 1 =$$

$$\frac{A + \exp n_2\varphi\varepsilon}{\exp n_2\varphi\varepsilon + A[\exp(n_1 + n_2)\varphi\varepsilon + 1] + A^2\exp n_1\varphi\varepsilon} \qquad (31)$$

In particular, at the equivalence point, it is equal

to $1/(1+A)$, which can also be seen by computing the reaction deficiency for $\phi=1$:

$$\zeta_{req} = \zeta_{req}' = \zeta_{eeq} = \frac{1}{1+A} \qquad (32)$$

Eqs. (26), (27), and (28) are not related to the titration fraction directly but only through the potential. Consequently, they can serve as working equations only if the relationship between ϵ and ϕ has been tabulated.

Approximate expressions for the relative reaction deficiencies in terms of the titration fraction can be obtained from the equilibrium constant expression

$$\exp(n_1 n_2 \varphi \Delta E_0) = \frac{\alpha n_1 + n_2}{(\phi-\alpha)^{n_1}(1-\alpha)^{n_1}} \qquad (33)$$

Substituting Eqs. (23) and (24) into Eq. (33) results in

$$\zeta_r = \frac{(1-\zeta_r)(n_1+n_2)/n_2}{(\phi-1+\zeta_r)^{n_1/n_2}}\exp(-n_1\varphi\Delta E_0) \qquad (34)$$

and

$$\zeta_r' = \frac{(\phi-\zeta_r')(n_1+n_2)/n_1}{(1-\phi+\zeta_r')^{n_2/n_1}}\exp(-n_2\varphi\Delta E_0) \qquad (35)$$

It is obvious that $\zeta_{req}>\zeta_r$, $\zeta_{req}=\zeta_{req}$, and $\zeta_{req}>\zeta_r'$ when $\phi>1$, $\phi=1$, and $\phi<1$, respectively. Therefore, Eqs. (34) and (35) can be approximated by

$$\zeta_r \fallingdotseq \frac{1}{(\phi-1)n_1/n_2 \, A^{\frac{n_1+n_2}{n_2}}} \qquad \text{for } \phi>1 \quad (34')$$

and

$$\zeta_r' \fallingdotseq \frac{\phi^{(n_1+n_2)/n_1}}{(1-\phi)^{n_2/n_1}A^{(n_1+n_2)/n_1}} \qquad \text{for } \phi>1 \quad (35')$$

respectively, as long as $|\phi-1|>\zeta_{req}$ is satisfied. In particular, when $E=E_1^0$ ($\phi \fallingdotseq {}^1/_2$)

$$\zeta_{r1}^{1/2} = \frac{1}{2A^{(n_1+n_2)/n_1}}$$

and when $E=E_2^0$ ($\phi \fallingdotseq 2$)

$$\zeta_{r2} = \frac{1}{A^{(n_1+n_2)/n_2}}$$

The approximate values of ζ_r for $\phi>1$ and ζ_r' for $\phi>1$ are conveniently evaluated by means of the following equation derived from Eqs. (23) and (24):

$$\zeta_r = \phi-1+\zeta_r' \qquad (36)$$

In the vicinity of the equivalence point, where het approximate equations do not apply, Eqs. (34) and (35) can be used for approximation. Thus, changing variable by

$$|\phi-1|=f\zeta \qquad (37)$$

Eq. (34), for example, becomes

$$(f+1)^{n_1/(n_1+n_2)} \quad \zeta_r=(1-\zeta_r)/A \fallingdotseq \frac{1}{A} \qquad (38)$$

Or

$$\frac{(f+1)^{n_1/(n_1+n_2)}}{f} \fallingdotseq \frac{1}{(\phi-1)A} \qquad \text{for } \phi>1 \quad (38')$$

When A is sufficiently large, unless extremely small values of $\phi-1$ is of interest, f is normally very large so that Eq. (38') can be approximated by

$$f \fallingdotseq [(\phi-1)A]^{(n_1+n_2)/n_2} \qquad (39)$$

which allows estimation of ζ for a given value of ϕ by using Eq. (37). Similar method can be used in approximating ζ_r' in the region where $\phi<1$.

In particular, when $\phi=1$, $\zeta_r=(\phi-1)=1/(A_2^{n_1/(n_1+n_2)})$ and $\zeta_r'=1-\phi=1/A_2^{n_2/(n_1+n_2)}$.

The value of f being estimated, the corresponding value of ϵ can be obtained by the following equation derived from Eq. (12):

$$\epsilon = \pm \frac{1}{n_1+n_2}\frac{1}{\varphi}\ln(f+1)$$
$$(+ \text{ for } \phi>1 \text{ and } - \text{ for } \phi<1) \qquad (40)$$

The rate of variation of th relative reaction deficiencies with the titration fraction can be estimated by the following equation derived from Eq. (33):

$$\frac{d\zeta_r}{d\phi} = -\frac{n_1(1-\zeta_r)\zeta_r}{n_1\phi\zeta_r+n_2(\phi-1+\zeta_r)} \qquad (41)$$

and

$$\frac{d\zeta_r'}{d\phi} = \frac{[n_1+n_2-n_1(\phi-\zeta_r')]\zeta_r'}{n_2\zeta_r+n_1(1-\phi+\zeta_r')\phi} \qquad (42)$$

Eqs. (23) and (24) give an usefull relationship between the two derivatives:

$$\frac{d\zeta_r}{d\phi} = \frac{d\zeta_r'}{d\phi} - 1 \qquad (43)$$

Changing the reaction deficiencies in the right-hand sides of Eqs. (40) and (41) results in

$$\frac{d\zeta_r}{d\phi} = -\frac{n_1(\phi-\zeta_r')(1-\phi+\zeta_r')}{n_2\zeta_r'+n_1\phi(1-\phi+\zeta_r')} \qquad (41')$$

and

$$\frac{d\zeta_r}{d\phi} = \frac{(\phi-1+\zeta_r)(n_2+n_1\zeta_r)}{n_1\phi\zeta_r+n_2(\phi-1+\zeta_r)} \qquad (42')$$

respectively. In particular, when $\phi=1$,

$$\frac{d\zeta_r}{d\phi} = -\frac{n_1}{n_1+n_2}(1-\zeta_{eq}) \qquad (41'')$$

and

$$\frac{d\zeta_r'}{d\phi} = \frac{n_2}{n_1+n_2} + \frac{n_1}{n_1+n_2}\zeta_{eq} \qquad (42'')$$

It is obvious that $\zeta_r<\zeta_{eq}$ when $\phi>1$ and $\zeta_r'<\zeta_{eq}$ when $\phi<1$. Therefore, each of Eqs. (41), (42), (41'), and (42') can be used for an approxmation in the region removed from the equivalence point. Those will provide useful criteria in photometric and amperometric determination of end point when incorporated with the volume factor. It should be noted that Eqs. (32)−(41'') have nothing to do with the Nernst expression but the equilibrium constant expression, and

hence they are applicable to any kind of equilibrium in a single phase. It may be pointed out that the relative rate of variation $\frac{1}{\zeta} \frac{d\zeta}{d\phi}$ would be more useful for some practical work.

Potentiostatic Buffer Index and Sharpness Index of Titration

It is most convenient mathematically to define the measure of the potentiostatic buffer capacity, the buffer index β, to be a derivative

$$\beta = -\frac{d\phi}{dE} = \frac{d\phi}{d\varepsilon} \tag{44}$$

Differentiating Eq. (19) with respective to ε gives for the index

$$\beta = \frac{\varphi[(n_1+n_2)\exp n_2\varphi\varepsilon + An_2\exp(n_1+n_2)\varphi\varepsilon + n_1A]\exp n_1\varphi\varepsilon}{(1+A\exp n_1\varphi\varepsilon)^2} \tag{45}$$

The sharpness index η defined as the magnitude of slope of the tittation curve is the inverse of β:

$$\eta = \frac{(1+A\exp n_1\varphi\varepsilon)^2}{\varphi[(n_1+n_2)\exp n_2\varphi\varepsilon + An_2\exp(n_1+n_2)\varphi\varepsilon + n_1A]\exp n_1\varphi\varepsilon} \tag{46}$$

which is independent of concentration, since ε depends on ϕ only (see Eq. (19)).

At the equivalence point, the sharpness index is given by

$$\eta_{eq} = \frac{1+A}{(n_1+n_2)\varphi} \tag{47}$$

Therefore, it is necessary to have A greater than $(n_1+n_2) \times 10^3$ in order to have $\Delta\phi$ less than 10^{-4} for about 100mv$\Delta\varepsilon$.

The sharpness of potentiometric end point depends strongly both A and n_1 and n_2 as Eq. (46) indicates. Thus, the minimum value of ΔE_0 for assuring reasonable accuracy of a redox titration depends strongly on n_1 and n_2. For example, the sharpness index of cerium (IV)-iron (II) titration is 1.2×10^7 ($A=9.25\times 10^8$), whereas that for permanganate-iron (II) is 2×10^9 ($A=4.68\times10^{11}$), while ΔE_0 is 1.06 and 0.83v, respectively.

In most problems, another expression of η derived in the following is more useful than Eq. (46). Thus, differentiating Eq. (12), after changing variables, with respect to ϕ results in

$$\eta_- = \frac{1}{(n_1+n_2)\varphi}\left[\frac{1}{\zeta'_r}\frac{d\zeta'_r}{d\phi} + \frac{1}{1-\phi+\zeta'_r}(1 - \right.$$

$$\left. \frac{d\zeta'_r}{d\phi})\right] \qquad \text{for} \qquad \phi<1 \tag{48}$$

and

$$\eta_+ = \frac{1}{(n_1+n_2)\varphi}\left[\frac{1}{\phi-1+\zeta_r}(\frac{d\zeta_r}{d\phi}+1)\right.$$

$$\left. -\frac{1}{\zeta_r}\frac{d\zeta_r}{d\phi}\right] \qquad \text{for} \qquad \phi>1 \tag{49}$$

Eliminating $\frac{d\zeta}{d\phi}$ using Eqs. (41) and (42) gives

$$\eta_- = \frac{1}{\varphi}\frac{1}{n_2\zeta_r' + n_1(1-\phi+\zeta_r')\phi} \tag{50}$$

and

$$\eta_+ = \frac{1}{\varphi}\frac{1}{n_1\phi\zeta_r + n_2(\phi-1+\zeta_r)} \tag{51}$$

Further modification can be made by using Eq. (37) as

$$\eta_- = \frac{1}{\varphi} \cdot \frac{f}{(1-\phi)[n_2+n_1(f+1)\phi]} \tag{50'}$$

and

$$\eta_+ = \frac{1}{\varphi} \cdot \frac{f}{(\phi-1)[n_1\phi+n_2(f+1)]} \tag{51'}$$

For the values of ϕ sufficiently removed from unity, so that $|\phi-1|>\zeta$ can be assumed, those equations may be approximated by

$$\eta_- \doteqdot \frac{1}{\varphi}\frac{1}{n_1\phi(1-\phi)} \tag{50''}$$

and

$$\eta_+ \doteqdot \frac{1}{\varphi}\frac{1}{n_2(\phi-1)} \tag{51''}$$

It can be shown readily from Eqs. (50) and (51) that the potential vs. titration fraction plot is not symmetric about the equivalence point.

Inflexion Point vs. Equivalence Point

The theorem of defferentials of inverse function applied to Eq. (19) gives

$$\frac{d^2\varepsilon}{d\phi^2} = -\frac{(1+A\exp n_1\varphi\varepsilon)^3}{\varphi\exp 2n_1\varphi\varepsilon} \cdot \left[n_2^2A^2\exp(2n_1 \right.$$

$$+n_2)\varphi\varepsilon + (2n_2^2+2n_1n_2-n_1^2) \cdot A\exp(n_1+n_2)$$

$$\varphi\varepsilon + (n_1+n_2)^2\exp n_2\varphi\varepsilon - n_1^2A^2\exp n_1\varphi\varepsilon + n_1^2A]/$$

$$[An_2\exp(n_1+n_2)\varphi\varepsilon + (n_1+n_2)\exp n_2\varphi\varepsilon + n_1A]^3 \tag{52}$$

The inflexion point on the titration curve will occur when the numerator of Eq. (52) equals zero. Evidently, the latter is nonzero at the equivalence point, including the cases when $n_1=n_2$. As long as the inflexion point in the vicinity of the equivalence point is of interest, it will be sufficient to consider the small values of ε only. For such cases, neglecting the third term in the parenthesis of che numerator, the approximate value of the potential at the inflexion point, ε_i, may be obtained by solving the following equation:

$$An_1^2c(2n_1+n_2)\varphi\varepsilon_i + (2n_2^2+2n_1n_2-n^2)$$
$$e^{(n_1+n_2)\varphi\varepsilon i} + n_1^2 = An_1^2e^{n_1\varphi\varepsilon i} \qquad (53)$$

Rearranging Eq. (53) gives

$$\frac{n_2^2}{n_1^2}\exp(n_1+n_2)\varphi\varepsilon_i = 1 - \frac{1}{An_1^2}[(2n_2^2 +$$
$$2n_1n_2-n^2)\exp n_2\varphi\varepsilon_i + n_1^2\exp(-n_1\varphi\varepsilon_i)] \qquad (53')$$

or

$$\varepsilon_i \doteq \frac{2}{(n_1+n_2)\varphi}\ln\frac{n_1}{n_2} + \frac{1}{(n_1+n_2)\varphi}\ln$$
$$\left[1 - \frac{2n_2^2+2n_1n_2-n^2_1}{n_1^2A}\exp n_2\varphi\varepsilon_i - \frac{1}{A}e^{-n_1\varphi\epsilon i}\right] \qquad (53'')$$

Since the second and third terms of the argument of logarithmic expression will be normally much smaller than unity, Eq. (53'') can be apporximated by

$$\varepsilon_i \doteq \frac{4.6}{(n_1+n_2)\varphi}\log\frac{n_1}{n_2} - \frac{1}{An^2_1(n_1+n_2)\varphi}$$
$$[(2n^2_2+2n_2n_1-n^2_1)\exp n_2\varphi\varepsilon_i + n^2_1\exp(-n_1\varphi\varepsilon_i)] \qquad (54)$$

Taking the first term of Eq. (54) as the zeroth order approximation, ε_i can be successively approximated. The first order approximation thus obtained is

$$\varepsilon_i \doteq \frac{4.6}{(n_1+n_2)\varphi}\log\frac{n_1}{n_2} - \frac{3n_2-n_1}{An^2_1\varphi}(n_1/n_2)^{(2n_2/n_1+n_2)} \qquad (54')$$

In particular, when $n_1=n_2$, the first term varnishes, indicating that ε_i is extremely small if A is sufficiently large. Thus, the exponential terms in Eq. (54) can be approximated by the power expansion up to linear term, which leads the equation to

$$\varepsilon_i \doteq \frac{2}{n_1(A-1)\varphi} \qquad (55)$$

Therefore, in the symmetric cases, the deviation of the inflexion point from the equivalence point is negligibly small as long as A is sufficiently large.

For the cases where $n_1 \doteqdot n_2$, substituting the first term of Eq. (54) into Eq. (19), such deviation can be estimated as

$$\phi - 1 = \frac{n^2_1/n^2_2 - 1}{1 + A(n_1/n_2)(2n_1/n_1 + n_2)} \qquad (56)$$

which will be of the order of $1/A$. Therefore, theoretically, the inflexion point of the potential curve can be considered to coincide with the equivalence point within experimental error, if A is greater than 10^5. However, in mannual potentiometric titration, graphical determination of the inflexion point does not necessarily give the true one. The error inherent to such procedure shall be analyzed elsewhere.

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