

산화환원 전위차적정에 있어 수치미분법으로 얻은 영 2 차미분 종말점의 오차*

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Errors in Potentiometric End-Point of Redox Titrations Determined by Zero Second Derivative Method*

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요 약. 산화환원 전위차 적정에 있어, 수치미분법으로 얻은 적정곡선의 2차 미분이 0이 되는 점을 얻어 종말점으로 삼을 때, 그 오차의 성격을 전자계산기를 사용하여 계산하였다. 그 결과로부터 당량점이 포함되는 시약첨가량의 어느 부분에 당량점이 존재하는가에 따라 종말점의 오차가 변화함을 알 수 있다. 오차는 그 중심점에서 당량점이 벗어남에 따라 증가하며 최대 오차는 첨가량의 약 $\frac{1}{2}$ 이다.

따라서 수치미분법으로 영 2차미분점을 얻는 경우에는 적정곡선의 최대 기울기의 점을 얻어 두 값을 비교해 보는 것이 바람직스럽다. 또 종말점 부근에서는 묽은 시약을 사용하여 적정하는 방법으로 오차를 작게 할 수 있다.

ABSTRACT. The potentiometric end-point of redox titrations determined by nulling the second derivative of the titration curve by numerical differentiation method is analyzed by using an electronic digital computer. The error involved in the method is shown to be dependent on the location of the equivalence point in the titrant addition increment that encompasses the latter. The error increases as the equivalence point moves away from the mid-point of the increment toward a maximum value that is as great as a half of the increment.

Therefore, when the numerical differentiation method is used to null the second derivative, the end-point should be compared with the steepest point of the titration curve or diluted titrant should be used in the vicinity of the end-point.

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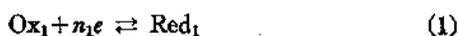
INTRODUCTION

In potentiometric redox titrations, it is an accepted practice¹ to determine the end-point by numerical differentiation method² assuming that the titration curve has the maximum slope at sufficiently close vicinity of the equivalence point. Recently, mathematical treatment^{3,4} of the potentiometric redox titration curve has ascertained validity of the above-mentioned assumption.

As pointed out in the previous report,^{4a} however, the numerical difference calculation does not necessarily give sufficiently accurate end point. No account of this situation has appeared in the literature. Because a large volume numerical computations can be carried out quite easily by using an electronic digital computer, it is now appropriate to locate the position of the inflexion point of the potentiometric redox titration curve that is obtained by numerical difference calculations. It is shown here that the error of end-point obtained by the numerical differentiation method can be fairly large.

GENERAL RELATIONSHIPS

Restricting ourselves to homogeneous redox reactions the following two reversible couples are considered:



for which the respective formal oxidation potentials are $E_1^{0'}$ and $E_2^{0'}$. The mathematical relationships used in the previous reports⁴ are briefly repeated here.

In the titration of V_0 liters of C_0 molar Red_1 ,

when V liters of C molar Ox_2 is added the equilibrium concentrations of the chemical species involved are given by, assuming the volume change to be negligible,

$$[\text{Red}_1] = \frac{C_0 V_0 (1 - \alpha)}{V + V_0} \quad (3)$$

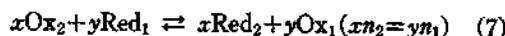
$$[\text{Ox}_1] = \frac{C_0 V_0 \alpha}{V + V_0} \quad (4)$$

$$[\text{Red}_2] = \frac{x C_0 V_0 \alpha}{y (V + V_0)} = \frac{C_0 V_0 \alpha}{V + V_0} \cdot \frac{n_1}{n_2} \quad (5)$$

$$[\text{Ox}_2] = \frac{C_0 V_0 (\phi - \alpha)}{V + V_0} \cdot \frac{n_1}{n_2} \quad (6)$$

$$\left(\phi = \frac{CV}{C_0 V_0} \cdot \frac{n_2}{n_1} \right)$$

where α designates the fraction of Red_1 converted to Ox_1 . The chemical reaction representing the titration reaction is



for which the equilibrium constant K is related to the formal potentials as

$$K = \frac{[\text{Ox}_1]^y [\text{Red}_2]^x}{[\text{Red}_1]^y [\text{Ox}_2]^x} = \frac{\alpha^{x+y}}{(\phi - \alpha)^x (1 - \alpha)^y} \quad (8)$$

$$\Delta E^{0'} = E_2^{0'} - E_1^{0'} = (RT / n_1 n_2 F) \ln K \quad (9)$$

where R , T , and F have their usual meaning.

The respective Nernst expressions for the half reactions (1) and (2) are given by

$$E = E_1^{0'} + \frac{1}{n_1 \phi} \ln \frac{\alpha}{1 - \alpha} \quad (10)$$

and

$$E = E_2^{0'} + \frac{1}{n_2 \phi} \ln \frac{\phi - \alpha}{\alpha} \quad (11)$$

where $\phi = \frac{F}{RT}$ ($= 38.92 \text{ volts}^{-1}$ at 25°C).

In order to obtain the potentiometric titration curve, it is necessary to know the value of α as a function of the titration fraction ϕ . When $n_1 = n_2$ (symmetric case) so that $x = y$, it is simple to compute α for given values of ϕ , since the equilibrium constant expression

$$K = \frac{\alpha^2}{(1-\alpha)(\phi-\alpha)} \quad (12)$$

is a quadratic equation of α with the physically meaningful root

$$\alpha = \frac{K(1+\phi) - \sqrt{K^2(1-\phi)^2 + 4K\phi}}{2(K-1)} \quad (13)$$

On the other hand, it is rather complicated to compute α for the reactions which are not symmetrical in coefficients. Fortunately, however, $\log\{\alpha/(1-\alpha)\}$ in Eq. (9) can be approximated by $\log\{\phi/(1-\phi)\}$ as long as the inflexion point of the titration curve is sufficiently close to the equivalence point as shown below. It has been pointed out that the deviation of the inflexion point from the equivalence point is the same order of magnitude as the value of the relative reaction deficiency $\mathcal{J} = \phi - \alpha$ at the equivalence point.^{4b,c} As the equilibrium constant

expression at the equivalence point can be written as

$$K^{1/(x+y)} = \frac{\alpha_{eq}}{1-\alpha_{eq}} = \frac{1-\mathcal{J}_{eq}}{\mathcal{J}_{eq}} \quad (14)$$

the relative reaction deficiency at the equivalence point can be approximated by

$$\mathcal{J}_{eq} \doteq \frac{1}{1+K^{1/(x+y)}} \doteq K^{-1/(x+y)} \quad (15)$$

as long as K is sufficiently large. Furthermore, the reaction deficiency has its maximum value at the equivalence point and decreases very rapidly in the vicinity of the equivalence point but its decreasing rate is rather small elsewhere.^{4b,c} The relevance of this statement is illustrated for several examples in Table 1. Thus, when $1-\phi$ is much larger than \mathcal{J} , Eq. (10) can be approximated by

Table 1. Variation of relative reaction deficiency, with titration fraction for selected values of equilibrium constant.

(a) $n_1 = n_2 = 1$

ϕ	K			
	10^{20}	10^{15}	7.18×10^{12} *	10^{10}
0.1	1.1×10^{-22}	1.1×10^{-17}	1.5×10^{-15}	1.1×10^{-12}
0.5	5×10^{-21}	5×10^{-16}	7×10^{-14}	5×10^{-11}
0.9	8.1×10^{-20}	8.1×10^{-15}	1.1×10^{-12}	8.1×10^{-10}
0.95	1.8×10^{-19}	1.8×10^{-14}	2.5×10^{-12}	1.8×10^{-9}
0.96	2.3×10^{-19}	2.3×10^{-14}	3.2×10^{-12}	2.3×10^{-9}
0.97	3.1×10^{-19}	3.1×10^{-14}	4.3×10^{-12}	3.1×10^{-9}
0.98	4.8×10^{-19}	4.8×10^{-14}	6.7×10^{-12}	4.8×10^{-9}
0.99	9.8×10^{-19}	9.8×10^{-14}	1.38×10^{-11}	9.8×10^{-9}
0.999	9.97×10^{-18}	9.97×10^{-13}	1.37×10^{-10}	9.97×10^{-8}
1.00	10^{-10}	3.16×10^{-8}	3.7×10^{-7}	10^{-5}

(b) $n_1 = 1, n_2 = 5, E_1^{0'} = 0.680, E_2^{0'} = 1.510; K = 1.524 \times 10^{70}$ **

ϕ	0.1	0.5	0.9	0.95	0.99	0.999	1.00
	1.1×10^{-76}	3.3×10^{-71}	6.7×10^{-66}	3.9×10^{-65}	6.3×10^{-61}	6.6×10^{-56}	2.0×10^{-12}

* Corresponds to the case of $\text{Ce}^{4+} + \text{Fe}^{2+}$ reaction where $E_2^{0'}$ and $E_1^{0'}$ are taken to be 1.440 volts and 0.680 volts, respectively.

** Corresponds to the titration of Fe^{2+} with MnO_4^- in acidic solution.

$$E = E_1^{0'} + \frac{1}{n_1\phi} \ln \frac{\phi}{1-\phi} \quad (16)$$

At the equivalence point, the potential has the value given by

$$E_{eq} = \frac{n_1 E_1^{0'} + n_2 E_2^{0'}}{n_1 + n_2} \quad (17)$$

Beyond the equivalence point ($\phi > 1$), \mathcal{E} is again smaller than \mathcal{E}_{eq} so that Eq. (11) can be approximated by

$$E = E_2^{0'} + \frac{1}{n_2\phi} \ln(\phi - 1) \quad (18)$$

For practically useful cases where the value of equilibrium constant K is sufficiently large so that the relative reaction deficiency is sufficiently small, Eqs. (16), (17), (18) should give values of potential at any value of titration fraction ϕ with negligible error.

NUMERICAL COMPUTATION

The value of potentials at various values of ϕ for Ce(IV) titration and permanganate titration of Fe(II) given by Eqs. (16), (17), and (18) are computed with FACOM 230 computer restricting to the range $0.9 \leq \phi \leq 1.1$. The interval $\Delta\phi$ was chosen to be 1/10, 1/20, 1/40 and 1/80 of the given range; *i.e.* the magnitude of $\Delta\phi$ chosen were 2/100, 1/100, 5/1000, and 25/10,000, respectively. For the given magnitude of $\Delta\phi$, the potentials were computed for varying relative positions of the increment with respect to the equivalence point and each position is designated by the ratio of the magnitudes of the two portions of the increment that encompasses the equivalence point as shown in Fig. 1.

RESULTS AND DISCUSSION

From the potential values, the value of ϕ at

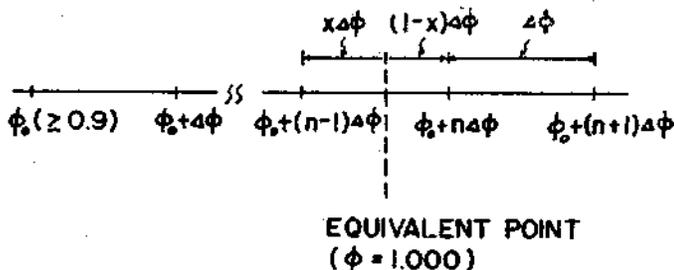


Fig. 1. Definition of the relative position of the titrant increment encompassing the equivalence point in terms of the fractional parameter x .

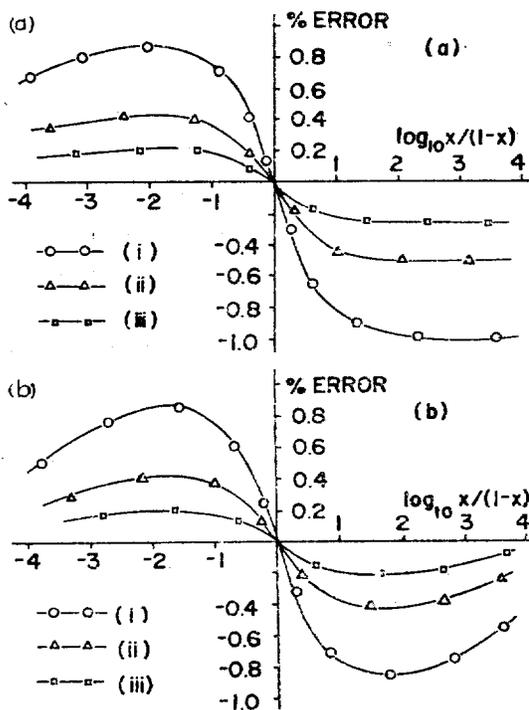


Fig. 2. End-point error as the function of the position of the equivalence point in the titrant increment encompassing it. (a): $Fe^{2+}-Ce^{4+}$ system; (b) $Fe^{2+}-MnO_4^-$ system. (i), (ii), and (iii) for the value of $\Delta\phi$ 0.02, 0.01, and 0.005, respectively.

which $\Delta^2 E / \Delta\phi^2$ equals zero was located by the computer for various values of the ratio $x/(1-x)$. The deviation of the so obtained end-point from unity is the relating titration error of numerical location of inflexion point. The results are summarized in Fig. 2. The

Table 2 Maximum value of the end-point error in relation to the magnitude of the titrant increment.

$\Delta\phi$	Increment		Maximum relative error, %	
	Volume of titrant*, ml		Fe ²⁺ + Ce ⁴⁺	Fe ²⁺ + MnO ₄ ⁻
0.02	1.0		±0.85	±0.99
0.01	0.5		±0.42	±0.49
0.005	0.25		±0.21	±0.25
0.0025	0.125		±0.10	±0.12

* When stoichiometric volume is 50.00 ml.

maximum errors observed for various magnitude of $\Delta\phi$ is give in Table 2.

In practical titrations, the smallest value of $\Delta\phi$ would be somewhere around 0.2% unless diluted titrant is used for incremental addition. Of course, there is a limit of dilution of the titrant because the indicator electrode cannot respond fast enough — not being poised. The maximum error of end-point in potentiometric redox titration determined by numerical differentiation method is about a half of the magnitude of the increment of titrant addition $\Delta\phi$. When the stoichiometric quantity of the titrant is about 50ml, $\Delta\phi=0.0025$ means that the titrant addition increment is 0.125 ml and the maximum titration error is expected to be +0.05 ml. However, in view of Table 1 and Eq. (18), the steepest potential change is confined to the range of the value of ϕ , in the interval from $1-0.001$ to $1+0.001$. Thus, in the worst case, the error can be greater than the end-point determined from the E vs. ϕ curve by visual location of the steepest point.

However, the value of x for each titration must be distributed randomly, and therefore, the average value of the end-points of several titrations should be appreciably smaller than the maximum value shown in Table 2. Nevertheless, it is always possible to encounter the maximum error when a single titration is employed.

In conclusion, although the second derivative zero can be very sharp in numerical difference computations, the zero point obtained is not necessarily the closest to the equivalence point, and the deviation can be as great as about a half the titrant increment. Thus, when the numerical differentiation method is used, it is desirable to repeat titrations several times or to use diluted titrant for the incremental addition, or at least to compare the second derivative zero end-point with the visually determined value of titrant volume of the steepest point of the potentiogram.

LITERATURE CITED

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