DAEAH HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 14, Number 4, 1970
Printed in Republic of Korea

A Theoretical Study of Oxidation-Reduction Titration Curves*

by

Q. Won Choi

Department of Chemistry, College of Liberal Arts and Sciences, Seoul National University

(Received July. 18, 1970)

산화·환원 적정곡선의 이론적 고찰

서울대학교 문리과대학
최 규 원

(1970. 7. 18 접수)

ABSTRACT

The variation of potential and completeness of reaction in an oxidation-reduction titration of Red_1 ($a\ Ox_1+n_1e \rightleftharpoons b\ Red_1$) by Ox_2 ($c\ Ox_2+n_2e \rightleftharpoons d\ Red_2$) is analyzed on the basis of general expressions. It is shown that the reaction deficiency as well as the rate of variation of the potential with titration fraction change in proportion to the $[n_2\ (a-b)-n_1\ (c-d)]$ th power of the concentration of the reagents. In particular, at the equivalence point, the expression of the potential contains a concentration dependent term that is proportional to $ac-bd$. Thus, the equivalence-point potential varies with the concentration of the reagents unless $ac=bd$ is satisfied.

It is also shown that the sharpness of the potentiometric end point is affected by exchanging titrand and titrant. The inflexion point of the potentiometric titration curve is shown to occur either prior to or after the equivalence point depending upon whether $n_1c < n_2b$ or $n_1c > n_2b$, the deviation being the same order of magnitude as the relative deficiency at the equivalence point.

INTRODUCTION

It has been pointed out that the equivalence-point potential in an oxidation-reduction titration deviates from the weighted average of the standard potentials and depends on the concentration of the reagents, except for the cases where the coefficients in both half-reactions are homogeneous[1),2)]. Furthermore, some aspects of the titration curve for inhomogeneous cases have been elucidated in terms of numerical data computed for particular examples[3)].

The present study is concerned with analyz-

* Presented in part at the 19th annual meeting of KCS, October, 1967.

ing the variation of equivalence-point potential on a general basis and investigating the various features of the titration curve for general cases.

BASIC EQUATIONS

Consider the titration of V_0 liters of C_0 molar solution of the reductant Red_1 up to V liters of C molar solution of the oxidant Ox_2. Attention will not be paid to the influence of the hydrogen ion and/or other ligands that may be involved in the titration reaction, because it can be included in the standard formal potentials, E_0's. Normally, it does not vary to an appreciable extent in the course of practical titrations. Let us assume that the potential throughout the titration is governed by the half-reactions of species 1 and 2:

$$aOx_1+n_1e \rightleftharpoons bRed_1;\ E^0{}_1 \quad (1)$$

$$cOx_2+n_2e \rightleftharpoons dRed_2;\ E^0{}_2 \quad (2)$$

Let the overall titrimetric reaction be

$$xcOx_2+ybRed_1 \rightleftharpoons xdRed_2+yaOx_1 \quad (3)$$

whence $xn_2=yn_1$ or $n_1/n_2=x/y$.

It will be assumed that the potential of the solution is governed by the concentration expressions of the Nernst equation throughout the titration; namely, the activity coefficients of the species involved can be taken care of by the respective standard formal potentials and kept almost constant:

$$E=E^0{}_1+\frac{1}{\varphi n_1}\ln\frac{[Ox_1]^a}{[Red_1]^b} \quad (4)$$

$$E=E^0{}_2+\frac{1}{\varphi n_2}\ln\frac{[Ox_2]^c}{[Red_2]^d} \quad (5)$$

where $\varphi=\frac{F}{RT}=38.95$ volt at 25C°.

Letting the fraction of Red_1 converted to Ox_1 be α at the equilibrium, the equilibrium concentrations of the chemical species involved in the titration reaction are written as the following:

$$[Red_1]=\frac{C_0V_0(1-\alpha)}{V_0+V} \quad (6)$$

$$[Ox_1]=\frac{C_0V_0\alpha}{V_0+V}\cdot\frac{a}{b} \quad (7)$$

$$[Red_2]=\frac{C_0V_0\alpha}{V_0+V}\cdot\frac{n_1d}{n_2b} \quad (8)$$

$$[Ox_2]=\frac{CV-\frac{n_1c}{n_2b}\cdot C_0V_0\alpha}{V_0+V} \quad (9)$$

Remembering that the titration fraction can be defined as

$$\phi=\frac{CVyb}{C_0V_0xc}=\frac{CVn_2b}{C_0V_0n_1c} \quad (10)$$

Eqs. (4) and (5) can be rewritten by use of Eqs. (6), (7), (8), (9) and (10) as

$$E=E^0{}_1+\frac{1}{n_1\varphi}\ln\frac{\alpha^a}{(1-\alpha)^b}+\frac{a}{n_1\varphi}\ln\frac{a}{b}+\frac{a-b}{n_1\varphi}\ln\frac{C_0C}{C+\frac{n_2bc_0}{n_1c}\phi} \quad (11)$$

and

$$E=E^0{}_2+\frac{1}{n_2\varphi}\ln\frac{(\phi-\alpha)^c}{\alpha^d}+\frac{1}{n_2\varphi}\ln\left(\frac{n_2b}{n_1d}\right)^d\cdot\left(\frac{n_1c}{n_2b}\right)^c+\frac{c-d}{n_2\varphi}\ln\frac{C_0C}{C+\frac{n_2bC_0}{n_1c}\phi} \quad (12)$$

Finally, multiplying Eq. (11) by n_1c and (12) by n_2b and adding results in

$$E=E^b{}_{eq}+S+B+K(C^0,\phi,\rho)+\left[\frac{ac-bd}{n_1c+n_2b}\ln\alpha+\frac{bc}{n_1c+n_2b}\ln\frac{\phi-\alpha}{1-\alpha}\right]\cdot\frac{1}{\varphi} \quad (13)$$

where

$$S=\frac{1}{(n_1c+n_2b)}\cdot\frac{1}{\varphi}\left[ac\ln a+(bd-bc-ac)\cdot\ln b+bc\ln c-db\ln d+b(d-c)\ln\frac{n_2}{n_1}\right] \quad (14)$$

$$B=\frac{(b-c)n_1n_2\Delta E_0}{(n_1+n_2)(n_1c+n_2b)}\quad(\Delta E_0=E^0{}_2-E^0{}_1) \quad (15)$$

$$\left.\begin{aligned}K(C_0,\phi,\rho)&=\frac{ac-bd}{(n_1c+n_2b)}\ln f(C_0,\phi,\rho)\\ f(C_0,\phi,\rho)&=\frac{C_0V_0}{V+V_0}=\frac{C_0}{1+\frac{n_2b}{n_1c}\phi\rho};\rho=C_0/C\end{aligned}\right\} \quad (16)$$

and

$$E^b{}_{eq}=\frac{n_1E^0{}_1+n_2E^0{}_2}{n_1+n_2} \quad (17)$$

It may be worthwhile to note that $f(C_0,\phi,\rho)=C_0$ when V can be considered to be zero as in coulometric titration, whence $\rho=0$. In the

following discussion, the subscripts eq, − and + will be used to designate the various regions of titration fraction; i.e., equivalence point, prior to and beyond the equivalence point, respectively. Eq. (13) is a generalized form of Eq. (15) in Bard and Simonsen's work[2], which is concerned with equivalence point only. The concentration dependence of potential is represented by the terms $K(C_0,\phi,\rho)$, $ln\ \alpha$ and $ln\ (\phi-\alpha)/(1-\alpha)$; α is a function of concentration and ϕ. When $ac=bd$ is satisified, the effect of the former two terms vanishes. In particular, if $a=b=c=d=1$, Eq. (13) is reduced to Eq. (12) of the previous work[4] on the cases of homogeneous reaction coefficients.

By defining the relative reaction deficiencies of Red_1 as

$$\left.\begin{aligned}\vartheta_r&=\phi-\alpha\\ \vartheta_r'&=1-\alpha\end{aligned}\right\}\qquad(18)$$

Eq. (13) can be rewritten as

$$E_-=E^0_{eq}+S+B+K(C^0,\phi,\rho)+\frac{ac-bd}{(n_1c+n_2b)\varphi}\cdot ln(\phi-\vartheta_r)+\frac{bc}{(n_1c+n_2b)\varphi}ln\frac{\vartheta_r}{l-\phi+\vartheta_r}\qquad(19)$$

and

$$E_+=E^0_{eq}+S+B+K(C_0,\phi,\rho)+\frac{ac-bd}{(n_1c+n_2b)\varphi}ln(1-\vartheta'_r)+\frac{bc}{(n_1c+n_2b)\varphi}ln\frac{\phi-1+\vartheta'_r}{\vartheta_r}\qquad(19')$$

which represent the potential as functions of titration fraction with a parameter ϑ_r or ϑ'_r.

The magnitude and rate of variation of the reaction deficiencies in relation to titration fraction can be elucidated on the basis of the equilibrium constant expression

$$A=exp(n_1n_2\varphi\Delta E_0)=F\cdot G\cdot\frac{\alpha^{an_2+dn_1}}{(1-\alpha)^{n_2b}(\phi-\alpha)^{n_1c}}\qquad(20)$$

where

$$\Delta E_0=E^0_2-E^0_1$$

$$F=[f(C_0,\phi,\rho)]^{n_2(a-b)-n_1(c-d)}\qquad(21)$$

and

$$G=a^{n_2a}.b^{n_1(c-d)-n_2a}\cdot c^{-n_1c}\cdot d^{n_1d}\cdot(n_2/n_1)^{n_1(c-d)}$$

In principle, Eq. (20) can be used in tabulating the relationships between α and ϕ or ϑ and ϕ for any given practical case, and in turn evaluation of potential at any desired titration fraction can be made, although the procedure may be quite cumbersome. On the other hand, an exact explicit expression of α or ϑ for general cases as a function of ϕ can not be obtained in a simple form. The values of ϑ obtained from Eq. (20) in the similar way as Bishop's method[2], which amounts to the use of an equation corresponding to Eq. (20) to compute the absolute reaction deficiency, may be substituted into Eqs. (19) or (19′) instead of the Nernst expression (11) or (12). In fact, when $1-\phi\gg\vartheta_r$ the Nersnt expression (11) can be approximated by

$$E_-=E^0_1+\frac{1}{n_1\varphi}ln\frac{\phi^a}{(1-\phi)^b}+\frac{a}{n_1\varphi}ln\frac{a}{b}+\frac{a-b}{n_1\varphi}ln\ f(C_0,\phi,\rho)+D\qquad(22)$$

where

$$D\fallingdotseq\frac{(a-b)\phi-a}{n_1\varphi\phi(1-\phi)}\vartheta_r\qquad(22')$$

Thus, when D is negligible, the only concentration dependent term is the fourth in the right-hand side of Eq. (22). It becomes independent of C when $a=b$, the half reaction of the titrand being homogeneous in coefficient. For example, if ferrous iron is titrated with dichromate, the titration curve for ϕ smaller than and not close to unity will be independent of concentration of reagents whereas titration of thiosulfate with iodine will result in the shifting of titration curve downwards by 2.303 RT/2F volts for every ten-fold dilution.

For the particular point, $\phi=\frac{1}{2}$,

$$E_{\frac{1}{2}}=E^0_1-\frac{a-b}{n_1\varphi}ln2+\frac{a}{n_1\varphi}ln\frac{a}{b}+\frac{a-b}{n_1\varphi}\cdot lnf(C_0,\frac{1}{2},\varphi)+D_{\frac{1}{2}}\qquad(22'')$$

The titration fraction where the potential is equal to E^0_1 satisfies

$$\ln\frac{(1-\phi+\vartheta_r)^b}{(\phi-\vartheta_r)^a}=a\ln\frac{a}{b}+(a-b)\ln f(C_0,\phi,\rho) \tag{23}$$

and where the potential is equal to E^0_2

$$\ln\frac{(1-\vartheta'_r)^d}{(\phi-1+\vartheta'_r)^c}=\ln\left(\frac{n_2b}{n_1d}\right)^d\cdot\left(\frac{n_1c}{n_2b}\right)^c+(c-d)\ln f(C_0,\phi,\rho) \tag{24}$$

respectively, in view of *Eqs.* (11) and (12). Therefore, if the reaction is practically quantitative throughout the titration, the E^0_1 point will shift towards and the E^0_2 point away from the equivalence point as the concentration decreases, for the cases where both $a-b$ and $c-d$ are positive and, vice versa. It is clear now that the main contribution to the influence on the titration curve comes from the concentration function $f(C_0,\phi,\rho)$ as long as the reaction is practically quantitative. It is obviously due to the fact that the potential depends on the reaction quotient whereas the titration fraction defines the concentration ratio; in other words, the position of the chemical equilibrium is determined by both the concentrations and concentration ratio unless the half reactions are homogeneous in coefficient. Eqs. (19) and (19′) represent one of the expressions that indicate the effect of concentration of reagents and the quantitativeness of titration reaction on the potential at given titration fraction.

It may be worthwhile to note that $f(C^0,\phi,\rho)=C_0$ when V can be considered to be zero as in coulometric titration whence $\rho=0$.

Unless there exists a particular relationship between the coefficients, the following equations are more convenient than Eqs. (19) and (19′) for computing the potential in terms of reaction deficiency, which are obtained by substituting Eq. (20) into (19) and (19′):

$$E_-=E^0_2+S+\frac{1}{n_2\varphi}\left[\frac{1nG}{b}+(c-d)\ln f(C_0,\phi,\rho)+c\ln\vartheta_r-d\ln(\phi-\vartheta_r)\right] \tag{19''}$$

and

$$E_+=E^0_1+S+\frac{1}{n_1\varphi}\left[\frac{1nG}{c}+(a-b)\ln f(C_0,\phi,\rho)-b\ln\vartheta'_r+a\ln(1-\vartheta'_r)\right] \tag{19'''}$$

EQUIVALENCE-POINT POTENTIAL

Letting $\phi=1$ in Eq. (13), the equivalence-point potential E_{eq} is obtained as

$$E_{eq}=E^h_{eq}+S+B+K_{eq}+\frac{ac-bd}{(n_1c+n_2b)\varphi}\ln\alpha_{eq} \tag{25}$$

or in an approximate form

$$E_{eq}=E^h_{eq}+S+B+K_{eq}-\frac{ac-bd}{n_1c+n_2b}\cdot\frac{\vartheta_{eq}}{\varphi} \tag{25'}$$

if the reaction is practically quantitative at the equivalence point.

In particular cases where $ac-bd$, Eq. (25) reduces to

$$E_{eq}=E^h_{eq}+S+B \tag{25''}$$

and all the concentration dependent terms vanish. Such a condition will be satisfied in many cases including the particular cases of $a=b=c=d$ and $a=d\neq b=c$. It is note worthy that there can be many cases where the equivalence-point potential is independent of the concentrations of reagents even when the coefficients of the half reactions are inhomogeneous, although there may be deviation from E^h_{eq} by a constant amount depending on relationship between the coefficients.

The general forms of each term appearing in Eq. (25) for several particular cases are listed in Table I. Whenever there is concentration dependence, i.e., $ac\neq bd$, the equivalence-point potential shifts by $\frac{bd-ac}{n_1c+n_2b}\cdot\frac{2.303}{\varphi}$ volts with every ten-fold dilution of the reagents. For example, in the titration of ferrous iron with dichromate where $a=b=c=1$, $d=2$, $n_1=1$ and $n_2=6$, it amounts to 8.5 mv and in the titration of thiosulfate with I_3, where $a=1$, $b=2$, $c=1$, $d=3$, and $n_1=n_2=2$, it amounts to 49.3mv. Thus, potentiometric titration up to a preassigned potential will be practical

only if $ac=bd$ is satisfied. The numerical example studied elsewhere[2] is compared with the figures obtained by using Eq. (25) neglecting the last term ($<10^{-3}$ mv) in Table 2.

As pointed out by Eq. (22″), $E_{\frac{1}{2}}$ also depends on the concentration of reagents. Thus, it will be useful to elucidate the concentration dependence of $E_{eq}-E_{\frac{1}{2}}$, $E_{\frac{3}{2}}-E_{eq}$ and $E_{\frac{3}{2}}-E_{\frac{1}{2}}$

TABLE 1. Terms representing shift of equivalence-point potential from E^0_{eq} in several particular cases

	Concentration S	independent terms B	Concentration K_{eq}	dependent terms other
$a=b=c=d$	0	0	0	0
$a=d\neq b=d$	$-\frac{(a-b)}{(n_1-n_2)\varphi}\ln\frac{n_2}{n_1}$	0	0	0
$a=b=d=d^*$ $ac=bd$	$\frac{0\quad 1}{(n_1c+n_2b)\varphi}\left[c\ln\frac{a^a}{b^b}+b\ln\frac{c^c}{d^d}+b(d-c)\ln\frac{n_2}{n_1}\right]$	$\frac{(b-c)n_1n_2\,\Delta E_0}{(n_1+n_2)\,(n_1c+n_2b)}$	0	0
$a=b=c\neq d$	$\frac{1}{(n_1+n_2)\varphi}\left[d\ln\frac{a}{d}+(d-a)\ln\frac{n_2}{n_1}\right]$			
$a\neq b=c=d$	$\frac{a}{(n_1+n_2)\varphi}\ln\frac{a}{b}$	0	$\frac{(a-d)}{(n_1+n_2)\varphi}\ln\frac{C_0c}{C+\frac{n_2C_0}{n_1}}$	$\frac{(a-d)}{(n_1+n_2)\varphi}\ln\alpha_{eq}$
$b=c\neq a\neq d$	$\frac{1}{\varphi(n_1+n_2)}\left[a\ln\frac{a}{b}+d\ln\frac{c}{d}+(d-c)\ln\frac{n_2}{n_1}\right]$			

* For the chemical reactions of well-known types, $a=b$ will mean $a=b=1$ and $c=d$ will mean $c=d=1$; thus $b=c$ so that $B=0$.

In view of Eqs. (25), (22″) and the similar equation for $E_{\frac{3}{2}}$ derived from Eq. (12), the following expressions are obtained.

$$E_{eq}-E_{\frac{1}{2}}=X(\rho)-\frac{b[n_2(a-b)-n_1(c-d)]}{n_1(n_1c+n_2b)\varphi}\ln C_0+\Delta \qquad (26)$$

$$E_{\frac{3}{2}}-E_{eq}=Y(\rho)-\frac{c[n_2(a-b)-n_1(c-d)]}{n_2(n_1c+n_2b)\varphi}\ln C_0+\Delta' \qquad (26')$$

$$E_{\frac{3}{2}}-E_{\frac{1}{2}}=Z(\rho)-\frac{n_2(a-b)-n_1(c-d)}{n_1n_2\varphi}\ln C_0+\Delta'' \qquad (26'')$$

where X, Y and Z are constants determined by a, b, c, d, n_1, n_2 and ρ, and Δ', Δ'', and Δ''' are small terms of the order of magnitude of the reaction deficiencies at $\phi=1$, $\phi=\frac{1}{2}$ and $\phi=\frac{3}{2}$, respectively. It is noteworthy that dilution of reagents not only results in a shift of titration curve as a whole but also widening the spacing between the two branches. Such an effect will affect the steepness of the titration curve in the vicinity of equivalence point, depending upon the sign and magnitude of $[n_2(a-b)-n_1(c-d)]/(n_1n_2\varphi)$.

TABLE 2. Comparison of computed data.

$C_0=C=0.05M$; $n_1=n_2,=2, a=2$, $b=c=1$ $d=3$; $\Delta E_0=100\ mv$; 30^0C. ($=38.26\text{Volt}^{-1}$), $n_2(a-b)-n_1(c-d)=6$.

(a) Potentials

Dilution factor	$(E_{eq}-E^0_2)^*$	Differences Eq. (25′)		$(E_{eq}-E_{\frac{1}{2}})^*$	Differences Eq. (26)	
1	61.598 mv	+15.0 mv	$\frac{2.303}{4\varphi}=$	96.882 mv	+45.00 mv	$\frac{3\times 2.303}{4\varphi}$
0.1	76.592	+15.0	15.0 mv	141.876	+45.00	45.0 mv
0.01	91.591			186.874		

(b) Reaction deficiency

Dilution factor	δ_{eq}*	ϑ_{eq} from Eq. (28)	δ_{eq} computed**
1	2.2075×10^{-5}	8.83×10^{-4}	2.23×10^{-5}
0.1	6.9963×10^{-6}	2.83×10^{-5}	7.01×10^{-8}
0.01	2.2126×10^{-10}	8.93×10^{-7}	2.23×10^{-10}

* Reference 2.

** ϑ_r is multiplied by the expected concentration at the equivalence point.

REACTION DEFICIENCIES

The knowledge of the relative reaction deficiency at the equivalence point is quite valuable because it will be the maximum value for the given system, and hence it will provide a criterion in making various approximations.

At the equivalence point, Eq. (20) can be written as

$$\frac{A}{F(1)G}=\frac{(1-\vartheta_{eq})an_2+dn_1}{\vartheta_{eq}n_2b+n_1c} \tag{27}$$

with

$$F(1)=\left[\frac{C_0}{1+\frac{n_2b}{n_1c}\rho}\right]^{n2(a-b)n1(c-d)}$$

Therefore, if $\vartheta\ll1$ can be assumed, the relative reaction deficiency at the equivalence point can be approximated by

$$\vartheta_{eq}\doteqdot\left[\frac{F(1)G}{A}\right]^{1/(n2b+n1c)} \tag{28}$$

and the absolute reaction deficiency at the equivalence point is given by

$$\delta_{eq}=\left[\frac{G}{A}\cdot\left\{\frac{C_0(1-\vartheta_{eq})}{1+\frac{n_2b}{n_1c}\rho}\right\}^{an_2+dn_1}\right]^{\frac{1}{n2b+n1c}}$$

$$=\left(1+\frac{n_2b}{n_1c}\right)^{-1}\cdot C_0\vartheta_{eq} \tag{28'}$$

Consequently, dilution of reagents will cause a decrease in relative reaction deficiency at the equivalence point if $n_2(a-b)-n_1(c-d)$ is positive, and vice versa. If $a=b$ and $c=d$, there will be no concentration effect on the relative reaction deficiency. The concentration dependence of reaction deficiencies is illustrated in Table 2.

The magnitude of the last term in Eq. (25′) can be estimated by Eq. (28).

If ϑ_{eq} is proven to be negligible in comparison to unity, Eq. (20) can be converted to

$$1n\vartheta_r\doteqdot-\frac{n_2\varphi\Delta E_0}{c}+\frac{1}{n_1c}1nG+\frac{1}{n_1c}\cdot 1n\frac{an_2+dn_1}{(1-\phi)^{n_2b}}+\frac{n_2(a-b)-n_1(c-d)}{n_1c}\cdot 1nf(C_0,\ \phi,\ \rho) \tag{29}$$

for the range prior to the equivalence point where $\vartheta_r\ll\phi$ and $\vartheta_r\ll1-\phi$, and

$$1n\ \vartheta'_r=-\frac{n_1\varphi\Delta E_0}{b}+\frac{1}{n_2b}1nG+\frac{n_2(a-b)-n_1}{n_2b}\cdot\frac{(c-d)}{}1nf(C_0,\ \phi,\rho)-\frac{n_1c}{n_2b}1n(\phi-1) \tag{29'}$$

beyond the equivalence point where $\phi-1\gg\vartheta'_r$ is satisfied. It is interesting to note that relative reaction deficiency decreases as dilution increases if $n_2(a-b)-n_1(c-d)$ is positive everywhere including the equivalence point. The concentration dependence of reaction deficiency is greater in the regions removed from equivalence point than at the equivalence point by a factor of $\frac{n_1c+n_2b}{n_1c}$ or $\frac{n_1c+n_2b}{n_2b}$, as comparison of Eqs. (29) and (29′) with Eq.(28) shows.

In the extreme vicinity of equivalence point, the relative reaction deficiency can not be neglected in comparison to $1-\phi$ or $\phi-1$ so that the approximate equations (29) and (29′) do not apply. The procedure developed in the previous work[4] introducing a parameter f by $1-\phi=f\vartheta_r$ for $\phi<1$ and $\phi-1=f\vartheta'_r$ for $\phi>1$ facilitates the calculation of reaction deficiency. Thus, from Eq. (20)

$$1n\vartheta_r=1n\vartheta_{eq}+\frac{1}{n_2b+n_1c}\cdot\Big[(an_2+dn_1)\ \ 1n(\phi-$$

$$\vartheta_r) - n_2 b \ln(f+1) + \ln\frac{F(\phi)}{F(1)}\Big] \qquad (31)$$

and

$$\ln\vartheta'_r = \ln'\vartheta_{eq} + \frac{1}{n_2 b + n_1 c} \cdot \Big[(an_2 + dn_1)\ \ln(1-$$

$$\vartheta'_r) - n_1\, c \ln(f+1) + \ln\frac{F(\phi)}{F(1)}\Big] \qquad (31')$$

Normally, relative reaction deficiencies will be negligible in comparison to ϕ or unity, thus allowing approximation of f from Eq. (31) or (31′) in conjunction with Eq. (30), and in turn reaction deficiencies. Namely,

$$\frac{1-\phi}{\vartheta_{eq}} \fallingdotseq f(f+1)^{-n_2 b/(n_2 b + n_1 c)} \qquad (32)$$

or

$$\frac{\phi-1}{\vartheta_{eq}} \fallingdotseq f(f+1)^{-n_1 c/(n_2 b + n_1 c)} \qquad (32)$$

is solved for f, and in turn f is used for calculating relative reaction deficiency by means of Eq. (30).

It should be noted that the procedure of calculating reaction deficiency given here has nothing to do with Nernst expression but based on the equilibrium constant expression. Therefore, it applies to any type of chemical equilibrium.

In order to have further information on reaction deficiency, it is desirable to compute its differential coefficient with respect to titration fraction. Differentiation of Eq. (20) after changing variable with respect to ϕ gives

$$\frac{d\vartheta_r}{d\phi} = 1 - \frac{\dfrac{n_2 b\rho[n_2(a-b) - n_1(c-d)]}{n_1 c + n_2 b\phi\rho} + \dfrac{n_1 c}{\vartheta_r}}{\dfrac{n_1 c}{\vartheta_r} + \dfrac{an_2 + dn_1}{\phi - \vartheta_r} + \dfrac{n_2 b}{1-\phi+\vartheta_r}} \qquad (33)$$

and

$$\frac{d\vartheta'_r}{d\phi} = -\frac{\dfrac{n_2 b\rho[n_2(a-b) - n_1(c-d)]}{n_1 c + n_2 b\phi\rho} + \dfrac{n_1 c}{\phi - 1 + \vartheta'_r}}{\dfrac{n_2 b}{\vartheta_r'} + \dfrac{n_1 c}{\phi - 1 + \vartheta_r'} + \dfrac{an_2 + dn_1}{1-\vartheta_r'}} \qquad (33')$$

It is easily shown that at equivalence point

$$\frac{d\vartheta_r}{d\phi} - \frac{d\vartheta_r'}{d\phi} = 1$$

and, if ϑ_{eq} is small enough,

$$\frac{d\vartheta_r}{d\phi} \fallingdotseq \frac{n_2 b}{n_2 b + n_1 c} \quad \text{and} \quad \frac{d\vartheta_r'}{d\phi} \fallingdotseq \frac{-n_1 c}{n_2 b + n_1 c}$$

which show no concentration dependence since the concentration dependent terms in the numerators of Eqs. (33) and (33′) are negligible compared to the inverse of relative reaction deficiency if the reaction is practically quantitative. In such cases, Eqs. (33) and (33′) can be approximated as

$$\frac{d\vartheta_r}{d\phi} \fallingdotseq \frac{n_2 b\vartheta_r}{n_2 b\vartheta_r + n_1 c(1-\phi+\vartheta'_r)} \qquad (34)$$

and

$$\frac{d\vartheta_r'}{d\phi} \fallingdotseq \frac{-n_1 c\vartheta_r'}{n_1 c\vartheta_r' + n_2 b(\phi - 1 + \vartheta_r')} \qquad (34')$$

in the extreme vicinity of equivalence point, and

$$\frac{n_1 c}{\vartheta_r} \cdot \frac{d\vartheta_r}{d\phi} \fallingdotseq \frac{an_2 + dn_1}{\phi} + \frac{n_2 b}{1-\phi} - \frac{n_2 b[n_2(a-b) - n_1(c-d)]\rho}{(n_1 c + n_2 b\phi\rho)} \qquad (35)$$

for $\phi < 1$, and

$$\frac{1}{\vartheta'_r} \cdot \frac{d\vartheta_r'}{d\phi} \fallingdotseq -\frac{n_1 c}{n_2 b(\phi - 1)} - \frac{[n_2(a-b) - n_1(c-d)]\rho}{n_1 c + n_2 b\phi\rho} \qquad (35')$$

for $\phi > 1$. It should be noted that the rate of change of the relative reaction deficiency in the extreme vicinity of equivalence point is of the order of unity and that in the region removed from equivalence point is the same order as the relative reaction deficiency. Furthermore, Eq. (35) indicates that reaction deficiency prior to equivalence point decreases with increasing ϕ if $n_2(a-b) - n_1(c-d)$ is positive, and vice versa. However, it increases with ϕ without regard to the sign of $n_2(a-b) - n_1(c-d)$ in the extreme vicinity of equivalence point. Therefore, reaction deficiency should pass through a minimum if the latter is positive. More detailed features can be seen by differentiating Eq. (29) with respect to ϕ; of course the result applies where Eq. (29) is valid. Thus, the root of Eq. (35) will give the position of the minimum ϑ_r. It should be noted that, if $\rho = 0$ or in

the case of internal generation of Ox_2 by electrolysis, $\frac{d\vartheta_r}{d\phi}$ will be always positive prior to the equivalence point regardless of the sign of $n_2(a-b)-n_1(c-d)$. On the other hand, Eq.(35′) indicates that ϑ_r' will go through a maximum in the region $\phi>1$.

The rate of variation of relation deficiency with respect to titration fraction depends on concentration of reagents implicitly through relative reaction deficiency itself.

Although $\frac{d\vartheta}{d\phi}$ is at most of the order of unity, relative rate of variation $\frac{1}{\vartheta}\cdot\frac{d\vartheta}{d\phi}$ will be very large when the reaction is practically complete. The completeness of reaction can be judged by computing ϑ_{eq} by using Eq.(28).

Differentiation of Eqs.(34) and (34′) gives

$$\frac{d^2\vartheta_r}{d\phi^2}=\frac{n_2b\ n_1c(n_2b+n_1c)\ (1-\phi+\vartheta_r)\vartheta_r}{[n_2b\vartheta_r+n_1c(1-\phi+\vartheta)]^3} \quad (36)$$

and

$$\frac{d^2\vartheta_r'}{d\phi^2}=\frac{n_2b\ n_1c(n_2b+n_1c)\ (\phi-1+\vartheta_r')\vartheta_r'}{[n_1c\vartheta_r'+n_2b(\phi-1+\vartheta_r')]^3} \quad (36')$$

respectively, which are both positive and of the order of $\frac{1}{\vartheta}$ whereas differentiation of Eqs. (35) and(35′) shows that $\frac{d^2\vartheta}{d\phi^2}$ are of the order of ϑ at the regions removed appreciably from the equivalence point. Thus, it is evident that the variation of $\frac{d\vartheta}{d\phi}$ is mostly concentrated around the equivalence point.

It should be noted that results on the study of relative reaction deficiency as a function of titration fraction given above apply to any chemical equilibrium, they are obtained from Eq.(20) only.

VARIATION OF POTENTIAL WITH TITRATION FRACTION

Differentiation of Eqs.(19) and(19′) gives

$$\frac{dE_-}{d\phi}=\frac{1}{(n_2b+n_1c)\varphi}\cdot\Big[-(ac-bd)\frac{n_2b\rho}{n_1c+n_2b\phi\rho}+(ac-bd)\frac{1}{\phi-\vartheta_r}(1-\frac{d\vartheta_r}{d\phi})+bc\frac{1}{\vartheta_r}\cdot\frac{d\vartheta_r}{d\phi}-\frac{bc}{1-\phi+\vartheta_r}(\frac{d\vartheta_r}{d\phi}-1)\Big] \quad (37)$$

and

$$\frac{dE_+}{d\phi}=\frac{1}{(n_2b+n_1c)\phi}\cdot\Big[-(ac-bd)\frac{n_2b\rho}{n_1c+n_2b\phi\rho}-(ac-bd)\frac{1}{1-\vartheta_r'}\cdot\frac{d\vartheta_r'}{d\phi}-\frac{bc}{\vartheta'_r}\cdot\frac{d\vartheta_r'}{d\phi}+\frac{bc}{\phi-1+\vartheta_r'}(1+\frac{d\vartheta_r'}{d\phi})\Big] \quad (37')$$

respectively. Those equations are convenient at the equivalence point only if $ac=bd$. Otherwise, the following equations obtained by differentiating Eqs.(19″) and(19‴) may be more convenient:

$$\frac{dE_-}{d\phi}=\frac{b(d-c)\rho}{(n_1c+n_2b\phi\rho)\varphi}+\frac{c}{n_2\varphi}\cdot\frac{1}{\vartheta_r}\cdot\frac{d\vartheta_r}{d\phi}+\frac{d}{n_2\varphi}\cdot\frac{1}{\phi-\vartheta_r}(\frac{d\vartheta_r}{d\phi}-1) \quad (38)$$

and

$$\frac{dE_+}{d\phi}=\frac{n_2b(b-a)\rho}{n_1(n_1c+n_2b\phi\rho)\varphi}-\frac{b}{n_1\varphi}\cdot\frac{1}{\vartheta'_r}\cdot\frac{d\vartheta_r'}{d\phi}-\frac{a}{n_1\varphi}\cdot\frac{1}{1-\vartheta_r'}\cdot\frac{d\vartheta_r'}{d\phi} \quad (38')$$

At the equivalence point, both types of equations give

$$\left(\frac{dE}{d\phi}\right)_{er}=\frac{bc}{\vartheta_{eq}}\cdot\frac{1}{n_1c+n_2b}\cdot\frac{1}{\varphi} \quad (39)$$

if ϑ_{eq} can be neglected in/comparison to unity. More explicitly $=\left(\frac{dE}{d\phi}\right)_{eq}=\left(\frac{A}{G}\right)\frac{1}{n_1c+n_2b}\cdot\left[\frac{n_1c+n_2b\rho}{n_1c\ C_o}\right]^{n_2(a-b)-n_1(c-d)}\cdot\frac{bc}{(n_1c+n_2b)\varphi}$ (39′)

Therefore, the steepness of titration curve at the equivalence point will depend on the concentration of reagents unless $n_2(a-b)-n_1(c-d)$ vanishes, which is in accordance with the qualitative anticipation from Eq.(26″). It is remarkable that, in view of Eq. (39′), if $a=b$ and $c=d$, even when ΔE_o is not large enough so that reaction deficiency at normal concentration is not sufficiently small, sharpness of potentiometric end point can be made greater by using more dilute solutions of reagents. In practice, however, response of indicating electrode bec-

omes slower with dilution of reagents and sets the limits on the effectiveness of dilution.

Differentiation of Eq.(38) and(38′) gives

$$n_2\varphi\frac{d^2E_-}{d\phi^2}=\frac{(n_2b\rho)^2(d-c)}{(n_1c+n_2b\phi\rho)^2}+\frac{c\left[\vartheta_r\frac{d^2\vartheta_r}{d\phi^2}-(\frac{d\vartheta_r}{d\phi})^2\right]}{\vartheta_r^2}$$

$$+\frac{d\left[(\phi-\vartheta_r)\frac{d^2\vartheta_r}{d\phi^2}+(\frac{d\vartheta_r}{d\phi}-1)^2\right]}{(\phi-\vartheta)^2} \qquad (40)$$

and

$$n_1\varphi\frac{d^2E_+}{d\phi^2}=\frac{(n_2b\rho)^2(b-a)}{(n_1c+n_2b\phi\rho)^2}-\frac{b\left[\vartheta_r'\frac{d^2\vartheta_r'}{d\phi_2}-(\frac{d\vartheta'}{d\phi}r)^2\right]}{\vartheta'^2_r}$$

$$-\frac{a\left[(1-\vartheta_r')\frac{d^2\vartheta_r'}{d\phi^2}-(\frac{d^2\vartheta_r'}{d\phi})^2\right]}{(1-\vartheta_r')^2} \qquad (40')$$

respectively. Substitution of values for $\frac{d\vartheta}{d\phi}$ given by Eq. (33) and for $\frac{d^2\vartheta}{d\phi^2}$ computed from Eq. (36) into Eqs. (40) results in

$$\varphi\left(\frac{d^2E}{d\phi^2}\right)_{eq}\frac{(n_2b\rho)^2\ (d-c)}{n_2(n_1c+n_2b\rho)^2}+\frac{n_1c-n_2b}{(n_2b+n_1c)^2}\cdot\frac{bc}{\vartheta^2_{eq}}$$

$$+\frac{n_1bcd}{(n_2b+n_1c)^2\vartheta_{eq}} \qquad (41)$$

and, similarly, using Eq. (33′), (36′) and (40′)

$$\varphi\left(\frac{d_2E_1}{d\phi_2}\right)_{eq}\doteqdot\frac{(n_2b\rho)^2\ (b-a)}{n_1(n_1c+n_2b\rho)^2}+\frac{n_1c-n_2b}{(n_2b+n_1c)^2}\cdot\frac{bc}{\vartheta^2_{eq}}$$

$$+\frac{n_2abc}{(n_2b+n_1c)^2\vartheta_{eq}} \qquad (41')$$

respectively; note that Eq. (40) and (40′) are exact but Eqs. (41) and (41′) are approximate formulas. (40′) are exatc but show that the major term is the same and its sign is determined by the term n_1c-n_2b.

In homogeneous case, where $a=b=c=d=1$, it was already noted that the inflexion point of potentiometric titration is located either beyond or prior to the equivalence point depending upon $n_1>n_2$ or $n_1\leq n_2$. (see Eq. (54′) of reference 4.) The abovementioned results show that the inflexion point is located prior to the equivalence point if $n_1c>n_2b$ and beyond the later if $n_1c<n_2b$. As pointed out at the end of the last section, $\frac{d\vartheta}{d\phi}$ varies mostly in the vicinity of the equivalence point. In view of Eqs. (38) and (38′), $\frac{dE}{d\phi}$ varies mortly in the same region, accordingly. Therefore, the approximate location of the inflexion point of the potentiometric titration curve can be obtained by substituting Eqs.(34) or (34′) into the second terms of Eqs. (41) or (41′) and putting the latter terms equal to zero. The results of such approximation are

$$1-\phi+\frac{n_2^2b^2-n_1^2c^2}{n_1^2c^2},\ \text{if}\ n_1c<n_2b \qquad (42)$$

and

$$\phi-1\doteqdot\frac{n_1^2c^2-n_2^2b^2}{n_2^2b^2},\ \text{if}\ n_1c>n_2b \qquad (42')$$

respectvely. Thus, the deviation of the inflexion point from the equivalence point is the same order of magnitude as ϑ_{eq}. Utilizing Eqs. (32) and (42), the deviation for the case where $n_1c<n_2b$ is obtained as

$$1-\phi\doteqdot\left[\frac{(n_1c)^{2(n_2b-1)}\cdot(n_2^2b^2-n_1^2c^2)}{(n_2b)_2{}^{n_2b}}\right]^{\frac{1}{n_2b+n_2c}}\cdot\vartheta_{eq} \qquad (42'')$$

which will be normally very close to ϑ_{eq}. In view of Eqs. (42″) and (28), the deviation of the inflexion point from the equivalent point depends on the ΔE^0 value as well as concentration of the reagent as long as $n_2(a-b)-n_1(c-d)$ does not vanish.

EFFECT OF EXCHANGING TITRANT AND TITRAND

For a given titration reaction represented by Eq. (3), if V^0 liters of C_0 molar solution of Ox_2 is titrated with V liters of C molar solution of Red_1, assuming the fraction of Ox_2 converted to Red_2 to be α', the following equations are obtained:

$$E=E^0{}_1+\frac{1}{n_1\varphi}1n\frac{\alpha'^a}{(\phi'-\alpha')^b}+\frac{1}{n_1\varphi}1n\left(\frac{n_2d}{n_1c}\right)^a\cdot\left(\frac{n_1c}{n_2b}\right)^b+\frac{a-b}{n_1\varphi}1nf(C_0,\ \phi',\ \rho) \qquad (43)$$

$$E=E^0{}_2+\frac{1}{n_2\varphi}1n\frac{(1-\alpha')^c}{\alpha'^d}+\frac{1}{n_2\varphi}1n\frac{c}{d}+\frac{c-d}{n_2\varphi}\cdot 1nf(C_0,\ \phi',\ \rho) \qquad (44)$$

$$E=E^h{}_{eq}+S'+B+K(C_0,\ \phi',\ \rho)+\frac{ac-bd}{(n_2b+n_1c)\varphi}\cdot$$

$$1n\alpha' + \frac{bc}{(n_2b+n_1c)\varphi} 1n \frac{1-\alpha'}{\phi'-\alpha'} \quad (45)$$

where

$$\phi' = \frac{CV\ n_1c}{C_0V_0n_2b}$$

$$S' = \frac{1}{(n_2b+n_1c)\varphi}\Big[-bc\ 1nb + (ac+bd-bc)1nc + (ac-bd)\,1nd - c(a-b)1n\frac{n_2}{n_1}\Big]$$

The equilibrium constant is represented by

$$A = \frac{\alpha'^{an_2+dn_2}}{(1-\alpha')^{n_1c}(\phi'-\alpha')^{n_2b}} \cdot F \cdot G'$$

where

$$G' = a^{n_2a} \cdot b^{-n_2b} \cdot c^{n_2b-n_2a-n_1d} \cdot d^{n_1d} \cdot \left(\frac{n_2}{n_1}\right)^{n_2(a-b)} \quad (46)$$

In particular, at the equivalence point, the following equations are satisfied:

$$E'_{eq} = E^k_{eq} + S' + B + K_{eq} + \frac{ac-bd}{(n_2b+n_1c)\varphi} 1n\alpha_{eq}' \quad (47)$$

$$\vartheta'_{eq} = 1-\alpha_{eq}' \fallingdotseq \left[\frac{F(1)\cdot G'}{A}\right]^{\frac{1}{n_2b+n_1c}} \quad (48)$$

$$\left(\frac{d\vartheta'}{d\phi'}\right)_{eq} \fallingdotseq \frac{n_1c}{n_2b+n_1c} \quad (49)$$

$$\left(\frac{dE}{d\phi'}\right)_{eq} = \frac{1}{(n_2b+n_1c)\varphi}\left[\frac{dK}{d\phi'} + \frac{ac-bd}{1-\vartheta'}\left(1-\frac{d\vartheta'}{d\phi'}\right) - \frac{bc}{\vartheta'}\right]_{eq} \fallingdotseq \frac{bc}{(n_2b+n_1c)\varphi} \cdot \frac{1}{\vartheta'_{eq}} \cdot$$

$$\fallingdotseq \frac{bc}{(n_2b+n_1c)\varphi} \cdot \left[\frac{A}{F(1)\cdot G'}\right]^{\frac{1}{n_2b+n_1c}} \quad (50)$$

From Eqs. (50) and (30)

$$\frac{\left(\frac{dE}{d\phi}\right)_{eq}}{\left(\frac{dE}{d\phi'}\right)_{eq}} \fallingdotseq \left[\frac{G'}{G}\right]^{\frac{1}{n_2b+n_1c}} = \left[\frac{n_2b}{n_1c}\right]^{\frac{n_2(a-b)-n_1(c-d)}{n_2b+n_1c}} \quad (51)$$

and from Eqs. (49) and (33)

$$\frac{\left(\frac{d\vartheta}{d\phi}\right)_{eq}}{\left(\frac{d\vartheta'}{d\phi'}\right)_{eq}} \fallingdotseq \frac{n_2b}{n_1c} \quad (52)$$

are obtained. It should be noted that n_2b/n_1c is the ratio of the coefficients of the titrands in the overall chemical equation (3).

Eqs. (51) and (52) indicate that the steepness of the potentiometric titration curves at the equivalence point takes different values when the titrand and titrant are exchanged in a given pair of reagents. In the potentiometric titration, the change of steepness depends on both the ratio n_2b/n_1c and the sign and magnitude of $n_2(a-b)-n_1(c-d)$. On the other hand, in spectrophotometric or amperometric titration, where the reaction deficiency is followed, it depends only on the ratio n_2b/n_1c.

Eqs. (45), (48) and (50) indicate that the concentration dependence of the titration curves is in the same direction as the reverse titration and determined by the sign of $n_2(a-b)-n_1(c-d)$

EFFECT OF BUFFERING ACTION ON AN REAGENT

In practical titrations, it is possible to have buffering action on one or more reagents involved in the oxidationreduction reaction. For example, in the titrations involving iodine solution the iodide concentration does not change appreciably. In such cases, the coefficient of the buffered reagent in the half reaction can be considered to be zero and the effects of the buffering reagents is included in the formal potential E. When a gaseous product or precipitate that dissolves sparingly in the solution is formed in the titration, the same will hold. Thus, the concentration dependence of the potential curve as well as the steepness of the curve at the equivalence point will be affected by buffering action on any reaction component by affecting the numerical values of $(ac-bd)$, $n_2(a-b)-n_1(c-d)$, G, F, and relative reaction deficiency.

LITERATURES CITED

1. A. J. Bard and S.H. Simonsen, *J. Chem. Ed.* **37**, 364(1960)
2. E. Bishop, *Anal. Chim. Acta* **27**, 253(1962)
3. E. Bishop, *ibid*, **26**, 397(1962)
4. Q. Won Choi, *J. Korean Chem. Soc.*, **11**, 159(1967)