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On the Titration Curves and Titration Errors in Donor Acceptor Titrations of Displacement and Electronic Transference Reactions

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Abstract

An overview of the state of the art concerning with earlier approaches to titration in redox systems is given in this chapter, in which an overview on redox bibliography has also been undertaken. Titration error has been the subject of a variety of excellent papers, but the number of papers dealing with titration error in redox titrations is scarce. However, a single hyperbolic sine expression for the titration error in donor/acceptor titration of displacement and electronic transference reactions is derived in this chapter. The titration error expression is applicable to symmetrical redox reactions, that is to say, those in which no polynuclear species are involved in the equilibria. The donor versus acceptor particle notation is chosen to accentuate the analogy with that used in the description of acids and bases following the steps given by the French School and other recognized authors (Budevsky, Butler, Charlot, Gauguin, Inczedy, Monnier, Rosset). A diagram for the titration error in function of the difference between the end and equivalence point (pX) is drawn in order to facilitate the graphical calculation of titration error. A detailed error analysis concerning with the propagation of systematic and random error propagation in the titration error is given.

Keywords: titration curves, titration error, electronic transference reactions

1. Introduction

Titrimetry constitutes one of the former analytical methods, been applied since the late eighteenth century [1]. Based on reaction chemistry, it is still developing [2–5] and continues to be extensively employed in several analytical fields as well as in routine studies [6] due to its simplicity, with little sacrifice in accuracy and precision, and low cost [7–9].

<i>T1</i>	<i>T2</i>	<i>T3</i>	<i>T SUM</i>	<i>E</i>	<i>pX</i>
1	1	1	3	1.3	21.667
1	1	1	3	1.35	22.5
1	1	1	3	1.4	23.333
1	1	1	3	1.45	24.167
1.1468	1.1468	1.1468	3.4403	1.5	25
2	2	2	6	1.51	25.167

Table 4. Titration curves of V(II) with MnO_4^- .

At the equivalence point

$$pe_{\text{eq}} = \frac{1}{z+y}(\log K_S + \log K_T) \quad (60)$$

The criterion of the quantitative titration can be deduced if we consider that the substance to be determined must be oxidized (or reduced) during the titration to an extent of 99.9% [23]. This means that the amount of determinant remaining untitrated at the equivalence point should not exceed 0.1% of that originally present, i.e.,

$$\log \frac{[\text{Ox}_S]}{[\text{Red}_S]} \geq 3 \quad (61)$$

and

$$pe_{\text{eq}} > (pe_{\text{eq}}^0)_S + 3\frac{1}{y} \quad (62)$$

$$(pe_{\text{eq}}^0)_S = \frac{1}{y} \log K_S \quad (63)$$

From Eqs. (60) and (63) also we obtain

$$y \log K_T - z \log K_S > 3(z+y) \quad (64)$$

If both oxidation-reduction systems in the titration involve two electrons, the difference between the $\log K$ values must be greater than 6.

In addition, if the oxidized or reduced product present in the solution containing the redox system takes part in a side-reaction, and the equilibrium position of this reaction can be kept constant, by maintaining suitable experimental conditions, the conditional oxidation-reduction constant, K' , can be deduced and used similarly to those used in complex chemistry

$$K' = \frac{[Red']}{[Ox'][e^-]^z} \quad (65)$$

$[Red']$ and $[Ox']$ are analytical concentrations without any respect to side-reactions. The connection between the conditional and real constants is the following one

$$K' = K \frac{\alpha_{Red(A)}}{\alpha_{Ox(B)}} \quad (66)$$

where $\alpha_{Red(A)}$ and $\alpha_{Ox(B)}$ are the side-reaction functions, and A and B denote the substances reacting with the reduced and oxidized substance, respectively.

$$\alpha_{Red(A)} = 1 + [L]\beta_1 + [L]^2\beta_2 + \dots \quad (67)$$

$$\alpha_{Ox(B)} = 1 + [L]\beta_1^* + [L]\beta_2^* + \dots \quad (68)$$

$[A]$ and $[B]$ are concentrations of the species reacting with the reduced and oxidized form, respectively, β 's and β^* 's are complex products or protonization constants products.

In all calculations concentration constants can be used if they are corrected to the corresponding ionic strength.

In practice, the most important side-reactions are complex formation and protonation. The oxidized and reduced form of a metal ion may form complexes of different stabilities with the complexing ligand L.

So, if the criterion of the quantitative determination is not fulfilled by a suitable pH change or by the use of a complexing agent that shifts the values of the conditional constants, the titration may be realized. For example, according to Vydra and Pribil [101], cobalt (II) can be titrated with iron (III) ions if 1,10-phenanthroline is added to the solution, and the pH is adjusted to 3 even though $K_{Co} \gg K_{Fe}$.

On the other hand, if another component present in the solution has similar oxidizing or reducing properties, then interfering species can be masked, so that the conditional redox constant of the interfering system is changed to such an extent that it no longer interferes with the main reaction.

5.1. Practical examples

(1) Calculate the pH necessary for the accurate direct titration of potassium hexacyanoferrate (III) with ascorbic acid, given that $\log K_{Fe(CN)_6} = 6.1$; the protonation constants of hexacyanoferrate(II) are $\log K_1 = 4.17$, $\log K_2 = 2.22$, $\log K_3 < 1$, $\log K_4 < 1$; the logarithms of all the protonation constants of hexacyanoferrate(III) are >1 . The equilibrium constant of the dehydroascorbic acid-ascorbinate redox system is $\log K_A = -2.5$; the protonation constants of the ascorbate ion are $\log K_1 = 11.56$ and 4.17 .

$$K_T' = K_T \frac{1}{\alpha_{\text{Ce-SO}_4}}, \quad \alpha_{\text{Ce-SO}_4} < 10^{7.2} \quad (77)$$

$$\alpha_{[\text{FeL}_2]^{+2}} = 1 + [\text{SO}_4^{-2}] \beta_1 + [\text{SO}_4^{-2}]^2 \beta_2 + [\text{SO}_4^{-2}]^3 \beta_3 \quad (78)$$

Thus, $[\text{SO}_4^{-2}]$ should be $< 0.39 \text{ M}$, to perform the titrimetry with accuracy.

6. Final comments

As a matter of fact redox titrations play a prominent role in volumetric analysis of redox actives species. A systematic study of the bibliography is undertaken in order to ascertain the state of the art concerning to redox titration curves. A method for the determination of titration error in donor/acceptor titrations of displacement and electronic transference reactions has been devised; a hyperbolic sine expression being derived for the titration error, applicable to symmetrical reactions (no polynuclear species being involved in one side of a half-reaction). The hyperbolic sine expression developed is compact and allows calculating the entire titration curve without piecemeal approximations, as usually occurs by dividing the titration curve in three parts: before, in, and beyond the equivalence point regions.

The method has been applied to some experimental systems characteristics of redox titration reactions. The method proposed is also applicable to mixtures of analytes, e.g., $\text{Fe(II)} + \text{Tl(I)}$, as well as to multistep redox titrations, e.g., $\text{V(II)/V(III)/V(IV)/V(V)}$ system. The forms of the redox titration curves are independent of the concentrations. However, when the concentrations involved are very low the responses of the electrodes are not appropriate. All calculations involved have been checked with the method proposed by "de Levie" [62] for the sake of comparison, and no differences were found in the numerical values obtained by both methods. A diagram for the titration error in function of the difference between the end and equivalence point (pX) is drawn in order to facilitate the graphical calculation of titration error.

Automatic titrators enable recording automatically the change with potential (E) or pH in titre during a given titration. The accuracy of the measurements can increase with the help of on-line microcomputer for the control and data acquisition, allowing among the possibility for curve-smoothing and differentiation.

The extension of the method to nonhomogeneous systems of the type $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$, I_2/I^- , or $\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}$ remains a challenge, this being a complex problem involving a complete reformulation of the presented equations, which implies a higher level of difficulty.

At the end of the chapter an appendix including a detailed study of the propagation of systematic and random errors on redox titration error has been carried out and spite of the complex expression obtained first on differentiation, the final expressions formulated were very compact. This topic is still under study and it will be dealt in further calculus.

Appendix

Error analysis

The exact calculation of standard deviations of nonlinear function of variables that are subject to error is generally a problem of great mathematical complexity. A linearization based on a Taylor expansion of the nonlinear portion of the expansion allows to obtain approximate estimates of standard deviations [102]; this approximation is quite adequate for most practical applications.

ΔT is a function of several variables, i.e. pX , $\log K_S$, $\log K_T$ all independent of each other. The systematic error present in pX , $\log K_S$, and $\log K_T$ are propagated to give an overall systematic error in a calculate quantity

$$E_{\text{sys}(\Delta T)} = \left(\frac{\partial \Delta T}{\partial pX} \right) E_{\text{sys}(pX)} + \left(\frac{\partial \Delta T}{\partial \log K_S} \right) E_{\text{sys}(\log K_S)} + \left(\frac{\partial \Delta T}{\partial \log K_T} \right) E_{\text{sys}(\log K_T)} \quad (79)$$

provided the errors $E_{\text{sys}(pX)}$, $E_{\text{sys}(\log K_S)}$, $E_{\text{sys}(\log K_T)}$ are small enough for higher order derivatives to be discarded.

For random error [103], the variance of ΔT can be calculated according to the propagation of variance

$$E_{\text{ran}(\Delta T)}^2 = \left(\frac{\partial \Delta T}{\partial pX} \right)^2 s_{pX}^2 + \left(\frac{\partial \Delta T}{\partial \log K_S} \right)^2 s_{\log K_S}^2 + \left(\frac{\partial \Delta T}{\partial \log K_T} \right)^2 s_{\log K_T}^2 \quad (80)$$

where s_{pX}^2 , $s_{\log K_S}^2$, and $s_{\log K_T}^2$ are the variances of the components pX , $\log K_S$, and $\log K_T$, respectively. The partial derivatives are taken, as before, as values equal or closest to the measured values.

For any measurement the total absolute error $E_{\text{abs}}(\Delta T)$ is related to the different types of error present by

$$E_{\text{abs}(\Delta T)} = \Delta T - \Delta \tau = E_{\text{ran}} + E_{\text{sys}} + E_{\text{bl}} \quad (81)$$

where ΔT is the value of the measurement, $\Delta \tau$ the true value, E_{rand} the random error, E_{sys} is the systematic error, and E_{bl} is the error due to blunders.

In any case, in order to know the proper error, it is necessary to know the standard deviation of the experimentally measured quantities, i.e., $E_{\text{sys}}(i)$ and s_i .

For the sake of convenience Eq. (22) may be put in the form

$$\Delta T = \frac{A}{1 + [X]^a K_S} [X]^p \sinh(C \Delta pX) \quad (82)$$

where

$$A = 2\sqrt{\frac{K_S}{K_T}} \quad (83)$$

$$p = \frac{a-b}{2} \quad (84)$$

$$C = \ln 10 \frac{a+b}{2} = \ln 10q \quad (85)$$

Make now

$$u = \frac{A[X]^p}{1 + [X]^a K_S} \quad (86)$$

and

$$v = \sinh(C\Delta pX) \quad (87)$$

in order to may differentiate easily ΔT against $d[X]$. Thus

$$\Delta T = uv \quad (88)$$

and we get for the derivative of a product

$$(\Delta T)' = u'v + v'u \quad (89)$$

The derivative of u will be given by

$$\begin{aligned} u' &= A \left(\frac{p[X]^{p-1}(1 + [X]^a K_S) - K_S a [X]^{a-1} [X]^p}{(1 + [X]^a K_S)^2} \right) = A \left(\frac{p[X]^{p-1}(1 + [X]^a K_S) - K_S a [X]^a [X]^{p-1}}{(1 + [X]^a K_S)^2} \right) \\ &= \frac{A[X]^{p-1}}{1 + [X]^a K_S} \left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} \right) \end{aligned} \quad (90)$$

On the other hand

$$v' = \cosh(C\Delta pX) C \frac{\partial(\Delta pX)}{\partial[X]} = \cosh(C\Delta pX) C \frac{\partial pX}{\partial[X]} = -\cosh(C\Delta pX) C \frac{1}{\ln 10[X]} \quad (91)$$

Taking into account Eqs. (87)–(91), we get

$$\frac{\partial \Delta T}{\partial[X]} = \frac{A[X]^{p-1}}{1 + [X]^a K_S} \left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} \right) \sinh(C\Delta pX) - \frac{A[X]^p}{1 + [X]^a K_S} \cosh(C\Delta pX) \frac{C}{\ln 10[X]} \quad (92)$$

and then

$$\frac{\partial \Delta T}{\partial [X]} = \frac{A[X]^{p-1}}{1 + [X]^a K_S} \left(\left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} \right) \sinh(C\Delta pX) - q \cosh(C\Delta pX) \right) \quad (93)$$

By multiplying through $[X]$ and taking into account Eq. (31) we get

$$[X] \frac{\partial \Delta T}{\partial [X]} = \frac{\Delta T}{\sinh(C\Delta pX)} \left(\left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} \right) \sinh(C\Delta pX) - q \cosh(C\Delta pX) \right) \quad (94)$$

and so

$$\frac{\partial \Delta T}{\partial pX} = -\ln 10 [X] \frac{\partial \Delta T}{\partial [X]} = \ln 10 \Delta T \left(q \coth(C\Delta pX) - \left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} \right) \right) \quad (95)$$

Eq. (22) may be presented in the form

$$\Delta T = \frac{2[X]^p}{\sqrt{K_T}} \frac{K_S^{1/2}}{1 + [X]^a K_S} \sinh(C\Delta pX) \quad (96)$$

Differentiation of Eq. (96) with respect to K_S gives

$$\frac{\partial \Delta T}{\partial K_S} = \frac{2[X]^p}{\sqrt{K_T}} \left(\left(\frac{\frac{1}{2} K_S^{-1/2} (1 + [X]^a K_S) - K_S^{1/2} [X]^a}{(1 + [X]^a K_S)^2} \right) \sinh(C\Delta pX) + \frac{K_S^{-1/2}}{(1 + [X]^a K_S)} \cosh(C\Delta pX) C \frac{\partial pX}{\partial K_S} \right) \quad (97)$$

On the other hand

$$\frac{\partial pX}{\partial K_S} = \frac{\partial \left(pX_{\text{end}} - \frac{\log K_T + \log K_S}{a + b} \right)}{\partial K_S} = \frac{-1}{a + b} \frac{\partial \log K_S}{\partial K_S} = \frac{-1}{(a + b) \ln 10 K_S} \quad (98)$$

$$C \frac{\partial pX}{\partial K_S} = \ln 10 \left(\frac{a + b}{2} \right) \frac{-1}{(a + b) \ln 10 K_S} = \frac{-1}{2K_S} \quad (99)$$

By combining Eqs. (97) and (99) we obtain

$$\frac{\partial \Delta T}{\partial K_S} = \frac{2[X]^p}{\sqrt{K_T}} \left(\left(\frac{\frac{1}{2} K_S^{-1/2} - \frac{1}{2} K_S^{1/2} [X]^a}{(1 + [X]^a K_S)^2} \right) \sinh(C\Delta pX) - \frac{\frac{1}{2} K_S^{-1/2}}{(1 + [X]^a K_S)} \cosh(C\Delta pX) \right) \quad (100)$$

which on rearranging gives

$$\frac{\partial \Delta T}{\partial K_S} = \frac{K_S^{-1/2}}{\sqrt{K_T}} [X]^p \left(\left(\frac{1 - K_S [X]^a}{1 + K_S [X]^a} \right) \sinh(C\Delta pX) - \cosh(C\Delta pX) \right) \quad (101)$$

Differentiating now ΔT against $\log K_S$ leads to

$$\begin{aligned}\frac{\partial \Delta T}{\partial \log K_S} &= \ln 10 K_S \frac{\partial \Delta T}{\partial K_S} = \frac{\Delta T}{2 \sinh(C \Delta pX)} \left(\left(\frac{1 - K_S [X]^a}{1 + K_S [X]^a} \right) \sinh(C \Delta pX) - \cosh(C \Delta pX) \right) \\ &= \frac{\ln 10}{2} \Delta T \left(\left(\frac{1 - K_S [X]^a}{1 + K_S [X]^a} \right) - \coth(C \Delta pX) \right)\end{aligned}\quad (102)$$

In order to differentiate ΔT against K_T we put (from Eq. (22))

$$\frac{\partial \Delta T}{\partial K_T} = \frac{2\sqrt{K_S}}{1 + [X]^a K_S} [X]^p \left(\frac{\partial}{\partial K_T} \left(\frac{1}{\sqrt{K_T}} \right) \cdot \sinh(C \Delta pX) + \frac{1}{\sqrt{K_T}} \cosh(C \Delta pX) C \frac{\partial \Delta pX}{\partial K_T} \right) \quad (103)$$

From Eqs. (18), (20), and (34), we get

$$C \frac{\partial \Delta pX}{\partial K_T} = \frac{-1}{2K_T} \quad (104)$$

By differentiating $1/\sqrt{K_T}$ against K_T in Eq. (52) and combining the resulting expression with Eq. (53) we get

$$\begin{aligned}\frac{\partial \Delta T}{\partial K_T} &= \frac{2\sqrt{K_S}}{1 + [X]^a K_S} [X]^p \left(\frac{-1}{2} K_T^{-\frac{3}{2}} \sinh(C \Delta pX) - \frac{-1}{2} K_T^{-\frac{3}{2}} \cosh(C \Delta pX) \right) \\ &= \frac{-\sqrt{\frac{K_S}{K_T}}}{K_T(1 + [X]^a K_S)} [X]^p (\sinh(C \Delta pX) + \cosh(C \Delta pX))\end{aligned}\quad (105)$$

As before with the case of $[X]$ and K_S , we may express the partial derivative of ΔT against $\log K_T$ as a function of the derivative against K_T and then

$$\begin{aligned}\frac{\partial \Delta T}{\partial \log K_T} &= \ln 10 K_T \frac{\partial \Delta T}{\partial K_T} = -\ln 10 \frac{\sqrt{\frac{K_S}{K_T}}}{1 + [X]^a K_S} [X]^p (\sinh(C \Delta pX) + \cosh(C \Delta pX)) \\ &= -\frac{\ln 10}{2} \frac{\Delta T}{\sinh(C \Delta pX)} (\sinh(C \Delta pX) + \cosh(C \Delta pX)) = -\frac{\ln 10}{2} \Delta T (1 + \coth(C \Delta pX))\end{aligned}\quad (106)$$

By combining Eqs. (28), (44), (51), and (55), we get for the standard deviation of systematic error

$$\begin{aligned}E_{\text{sys}}(\Delta T) &= \ln 10 \Delta T \left(\left(\frac{p - a K_S [X]^a}{1 + [X]^a K_S} - q \coth(C \Delta pX) \right) \right) E_{\text{sys}}(pX) \\ &+ \frac{1}{2} \left(\frac{1 - K_S [X]^a}{1 + K_S [X]^a} - \coth(C \Delta pX) \right) E_{\text{sys}}(\log K_S) - \frac{1}{2} (1 + \coth(C \Delta pX)) E_{\text{sys}}(\log K_T)\end{aligned}\quad (107)$$

In the same way, from Eqs. (29), (44), (51), and (55), we may obtain the variance of the random error

$$E_{\text{rand}}^2(\Delta T) = \ln^2 10 \Delta T^2 \left(\left(\frac{p - aK_S[X]^a}{1 + [X]^a K_S} - q \coth(C\Delta pX) \right)^2 s_{pX}^2 + \frac{1}{4} \left(\frac{1 - K_S[X]^a}{1 + K_S[X]^a} - \coth(C\Delta pX) \right)^2 s_{\log K_S}^2 + \frac{1}{4} (1 + \coth(C\Delta pX))^2 s_{\log K_T}^2 \right) \quad (108)$$

Note that in spite that relative complex expressions are involved in the required differentiations carried out with the purpose to propagate the systematic and random errors implied in the donor/acceptor titration, the algebra involved is simple, and the final expressions obtained are compact.

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