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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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Additional information is available at the end of the chapter

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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].

Titrimetry is a fast technique easily automated and cheap in terms of equipment. It is together with gravimetry one of the two special existing methods to determine chemical composition on the basis of chemical reactions (primary method) being used for methodological and working levels [10, 11]. Independent values of chemical quantities expressed in SI units are obtained through gravimetry and titrimetry (classical analysis). In titrimetry the quantity of tested components of a sample is assessed through the use of a solution of known concentration added to the sample which reacts in a definite proportion. The reaction between the analyte and the reagent must be fast, complete (with an equilibrium constant very large), proceed according to a well-defined (known stoichiometry) chemical equation (without side-reactions), lead to a stable reaction product, and usually, and take place in solution, although in some cases precipitation reactions are involved. To identify the stoichiometric point, where equal amounts of titrant react with equal amounts of analyte, indicators are used in many cases to point out the end of the chemical reaction by a color change. The indicator reacts with either the analyte or the reagent to produce (in a clear and unambiguous way) a color change when the chemical reaction has been completed.

This is known as the “end point” of the titration, which should be as close as possible to the equivalence point. The difference between the end point and the equivalence point is the titration error. In order to reduce the uncertainty in the results, the end point can also be detected by instrumental rather than visual means, i.e., by potentiometry, where the potential difference is measured between a working electrode and a reference electrode; in photometry, where the light transmission is measured with a photometric sensor; or in coulometric, where the titrant is generated electrochemically and the amount of titrant is calculated from the current and time of reaction using Faraday's law.

Titrimetric methods are classified into four groups depending on the type of chemical reaction involved: acid-base, oxidation-reduction, precipitation, and complexometric. Among the most common applications of titrimetry are the measurement of anionic and cationic species, and neutral molecules of both organic and inorganic substances. Although it has been extensively used for the measurement of pure substances, it also performs well when trace constituents in complex matrices want to be evaluated.

Before the experience, the titrant is standardized by titration of the primary standard, which must be stable against the influence of light, air, and temperature. The main primary standards are potassium hydrogen phthalate (KHP), benzoic acid, tris(hydroxymethyl)aminomethane (TRIS, THAM), or Na_2CO_3 for acid-base titration, As_2O_3 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{K}_2\text{Cr}_2\text{O}_7$, or KIO_3 for redox titration, NaCl for precipitation titrations, and CaCO_3 , $\text{Pb}(\text{NO}_3)_2$, Zn , Ni or Cu for complexometry. During the experience, the temperature should be constant (for ordinary work $\pm 0.5^\circ\text{C}$). To reduce the overall uncertainty, titrimetry can also be performed on a mass/mass basis using a weight burette with a primary standard.

Titrimetric methods can also be classified based on the properties of the reaction: if the assay is performed with a known concentration of titrant or with an unknown concentration of titrant is called direct or indirect titration, respectively, whereas back titration involves an excess of titrant that reacts until the equivalence with a known concentration of sample.

2. Titration in redox systems: earlier approaches

Redox titrations were essential in volumetric analysis as well as in electrometric techniques. The first attempts to quantify titration curves, including redox systems, and data processing [12] were from 1920s to 1930s. As suggested by Goldman's review [13], the first theoretical developments were due to Kolthoff [14], who provided the link between the application of physical chemistry and titrimetry [15–17] (though it was criticized by his Dutch colleagues in his earlier career). The understanding of redox equilibria provided the platform to the development on electrode processes [13].

One can plot against pE (or p_e) as variable either the logarithm of the concentration (or activity) of each species (maintaining the other concentration constant) or the logarithm of the ratio of the concentration (or activity) of the species [13] using as a reference one oxidation state. Then, the diagram, entirely composed of straight lines, is simple and easy to construct [18]. From \log (concentration) versus E diagrams redox titrations may be drawn [19–22], even the titration error by an appropriate modification [23, 24]. In fact, logarithmic diagrams, introduced by Bjerrum [25], have found a wide use in the study of titration systems, mainly in the acid-base domain [23, 26, 27]. On the basis of logarithmic diagrams, Maccà and Bombi [28] discuss the symmetry properties of titration curves and the linearity of Gran plots. In the particular case of redox systems, distribution diagrams are not as commonly used as they are for acid-base and complex ion systems [18, 29–31].

In 1960s titration was revisited to improve formulation of titration curves, in the papers by Bard and Simonsen, Bishop and Goldman's papers as indicated in the review of Goldman [13], "formal" potentials, E'_{0ir} being used in those approaches instead of standard potentials. de Levie [32–34] pointed out the similarity between the profile of redox and acid-base titration curves, related to a polyprotic acid titrated with NaOH. Equivalence points were also discussed. Some further papers were related to redox indicators and titration errors.

Anfält and Jagner [35] reviewed and evaluated the accuracy and precision of some frequently potentiometric end-point indicator methods. Yongnian and Ling [36] used mathematical methods to assess the application and advancement of titration methods. Although it is common to find examples of applications to redox titrations [37, 38] their actual use in redox titrations has been scarce [39–42]. The Gran methods were modified later [43–45], without unnecessary simplifications.

The most common topics dealing redox titrations and published in the last two decades were: to calculate stoichiometric point potentials by different types of redox titration [46]; the use of linear regression analysis of potentiometric data through linearization of the titration function [47, 48]; approximated titration curves [49] by logarithmic function studying the prediction of random error in titration parameters [50]; as well as the factors affecting the accuracy [51] of redox titrations. Nonlinear regression analysis allows the simultaneous evaluation of several parameters from the data obtained [52] in a single redox titration. A general algorithm and a program for the calculation and construction of titration curves [53] have been proposed. Numerical and computer simulations [54, 55] and equations by nonlinear

least squares with novel weighting functions [56] for redox potentiometric data were also evaluated.

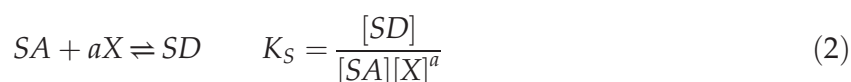
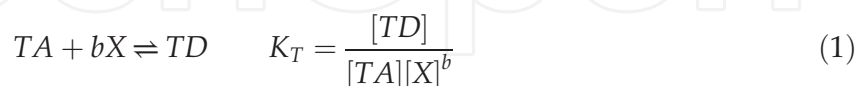
The analogy between acid-base and redox-behavior, as particle exchange reactions (of protons or electrons, respectively) [57, 58], has been interpreted through the years [59–67].

Titration error has been the subject of excellent publications, but the number of papers dealing with redox titration error is relatively scarce. The focus has been mainly put in acid-base, precipitation, and complex formation reaction titrations. In this chapter, an attempt is given to devise a titration error theory applicable to donor-acceptor titration of displacement and electronic transference (redox) reactions. The error will be formulated as a function of the titration parameters, in a hyperbolic sine expression way. As a matter of fact a detailed treatment of the analysis error issue is also carried out. The error analysis requires differentiating with respect to given variables leading at first sight to complex expressions, which at the end finally appears to be compact.

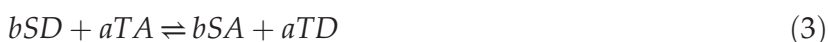
3. On the titration error in donor/acceptor titrations of displacement and electronic transference reactions

Acid-base, complexation, and precipitation titrations have been extensively dealt with both in scientific and educational literature. Redox titrations, although being of primary importance, have received less attention [68]. Titration error has been the subject of several excellent papers, the emphasis being placed, however, mainly on acid-base [69–73] as well as on precipitation [74–79], and complex formation titration reactions [80, 81]. A number of papers dealing with the topic of titration error in redox titration [13, 24, 82, 83] have also been appeared. Redox titrations hold an important place in simple, fast, low-cost analysis of redox-active-species [56]. In this chapter, a single equation is presented for symmetrical reactions for which the reduced and oxidized species of each half-reaction should be the same. Therefore the treatment is not strictly valid for such couples as $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ or I_2/I^- [81].

Let SD be a particle donor (weak or strong), to be titrated with a particle acceptor TA . The analyst can choose the titrant and will always use a strong one to obtain better results. The systems implied in the titration reaction and their corresponding equilibrium constants will be given by



X being the particle transferred in the semi-reactions involved in the global titration reaction



to which corresponds the following equilibrium constant

$$K_{eq} = \frac{[SA]^b [TD]^a}{[SD]^b [TA]^a} = \frac{K_T^a}{K_S^b} \quad (4)$$

Proton free equilibria are assumed first in the presentation for the sake of clarity though redox equilibria that are independent of pH are relatively few. Effects of such factors as hydrogen ion concentration and complexing ligands may be easily incorporated [84] in the corresponding conditional constants. The particle X may be a proton, electron, cation, or an uncharged molecule. This notation is chosen to accentuate the analogy with that used in the description of acids and bases by the French School and other recognized authors [19, 29–31, 85–92]. Anyway, as TA is a strong particle acceptor, it must occur that $K_T \gg K_S$.

From Eq. (3) it is readily seen that in any moment of the titration it holds that (through the entire concentration range)

$$b[TD] = a[SA] \quad (5)$$

On the other hand, we may define the (relative) titration error as

$$\Delta T = \left(\frac{bC_T - aC_S}{aC_S} \right)_{\text{end}} = T - 1 \quad (6)$$

where C_T and C_S are the analytical concentrations of titrant and analyte, respectively,

$$C_T = [TA] + [TD] \quad (7)$$

$$C_S = [SA] + [SD] \quad (8)$$

and T , the fraction titrated, is defined as the ratio between the amount of titrant added and the initial amount of analyte at any moment of the titration. Thus, depending on the nature of the titration, ΔT might be either positive or negative. When the titration is carried out in the reverse order the same result is obtained, but the equation now bears a minus sign.

Therefore, from Eqs. (6)–(8), it follows that

$$\Delta T = \left(\frac{b[TA] - a[SD]}{aC_S} \right)_{\text{end}} \quad (9)$$

By combining Eqs. (5) and (1), we have

$$[TA] = \frac{a}{b} \frac{[SA]}{K_T[X]^b} \quad (10)$$

and from Eq. (2) we obtain

$$[SD] = K_S[SA][X]^a \quad (11)$$

By substituting the values of $[TA]$ and $[SD]$ given by Eqs (10) and (11)

$$\Delta T = \frac{[SA]}{C_S} \left(\frac{1}{K_T[X]^b} - K_S[X]^a \right) \quad (12)$$

As the molarity fraction of the species $[SA]$ is given by

$$f_{SA} = \frac{[SA]}{C_S} = \frac{1}{1 + [X]^a K_S} \quad (13)$$

Eq. (12) may be transformed into

$$\Delta T = \frac{1}{1 + [X]^a K_S} \left(\frac{1}{K_T[X]^b} - K_S[X]^a \right) \quad (14)$$

By multiplying and dividing the right hand side of Eq. (14) by $\sqrt{(K_S/K_T)}$ we get

$$\Delta T = \frac{\sqrt{\frac{K_S}{K_T}}}{1 + [X]^a K_S} \left(\frac{1}{\sqrt{K_T K_S} [X]^b} - \sqrt{K_T K_S} [X]^a \right) \quad (15)$$

In the equivalence point, when the exact stoichiometric amount of titrant has been added, in addition to Eq. (15), the following condition is satisfied

$$a[SD] = b[TA] \quad (16)$$

and then, from Eqs. (1) and (2), it follows that when the exact stoichiometric amount of titrant has been added

$$\sqrt{K_T K_S} = \frac{1}{[X]_{eq}^{(a+b)/2}} \quad (17)$$

$$pK_{eq} = \frac{\log K_T + \log K_S}{a + b} \quad (18)$$

and then, the potential at the equivalence point is independent of the concentration of the reactants and thus unaffected by dilution. Note, however, that Eq. (18) is not perfectly general, because the simple relation of Eq. (16) for reactants and products is not always valid. The species involved in the equilibria may be polynuclear. The p^X in this instance varies with dilution.

By substituting Eq. (17) into Eq. (15)

$$\Delta T = \frac{\sqrt{\frac{K_S}{K_T}}}{1 + [X]^a K_S} [X]^{(a-b)/2} \left(\left(\frac{[X]_{eq}}{[X]} \right)^{(a+b)/2} - \left(\frac{[X]}{[X]_{eq}} \right)^{(a+b)/2} \right) \quad (19)$$

A chemical error will arise because of lack of agreement between the end point and equivalence point. The difference between the end point and the equivalence point of a titration is the source of systematic error of determination. Taking into account that

$$\Delta pX = pX_{end} - pX_{eq} \quad (20)$$

and

$$\sinh x = \frac{e^x - e^{-x}}{2} \quad (21)$$

after some manipulation, the following expression may be easily obtained

$$\Delta T = \frac{2\sqrt{\frac{K_S}{K_T}}}{1 + [X]^a K_S} [X]^{(a-b)/2} \sinh \left(\ln 10(a+b) \frac{\Delta pX}{2} \right) \quad (22)$$

or

$$\Delta T = W \sinh \left(\ln 10(a+b) \frac{\Delta pX}{2} \right) \quad (23)$$

where the shape coefficient W is depending on the particle concentration in the end point titration when asymmetrical titrations are being considered

$$W = \frac{2\sqrt{\frac{K_S}{K_T}}}{1 + [X]^a K_S} [X]^{(a-b)/2} \quad (24)$$

Low values of the stoichiometric coefficients a , b , as well as low difference $a-b$ values, and large K_T values lead to lower errors.

In the vicinity of the equivalence point, $+1 \gg [X]_{end}^a K_S$ and so

$$W = 2\sqrt{\frac{K_S}{K_T}} [X]_{end}^{(a-b)/2} \quad (25)$$

In those cases in which the titration reaction is symmetrical, $a = b$, and then

$$W = 2\sqrt{\frac{K_S}{K_T}} \quad (26)$$

and the following formula is obtained for the titration error

$$\Delta T = 2K_{\text{eq}}^{-1/(2a)} \sinh(\ln 10 a \Delta pX) \quad (27)$$

Note that the titration error may be formulated as a hyperbolic sine expression. Hyperbolic functions are of great worth in parameter estimation as shown by Asuero [93].

The methodology developed in this section of the chapter is going to be applied forward to some experimental situations characteristics of redox titration reactions. The calculations made by the hyperbolic sine method are checked with the procedure devised by de Levie [21, 26, 62]. A detailed treatment of systematic and random errors associated with the titration error is carried out in the following.

Note that the equations developed in this contribution can easily take into account the lateral reactions by using the corresponding lateral reaction coefficients and the conditional constants involved. A condition is however required, namely that the pH remains constant in the course of titration, which cannot always be achieved. Michalowski [4, 94–100] has given a general and definitive solution to the problem of redox equilibria, which does not require any restriction.

The beginnings of the rigorous GATES/Generalized Electron Balance (GEB) approach of Michalowski, which can be interpreted as a new natural law, dates back from 1992 to 1995. This approach has recently been shown repeatedly in the bibliography solving complex chemical problems and requires the use of nonlinear regression and a high level language such as MATLAB. The equations developed here, although very modest, have an obvious didactic interest and can be seen in the case of the redox equilibria as an alternative route to that given by de Levie [62].

4. Electronic transfer reactions

In the following, some titration curves of typical oxide-reduction reactions, involving Ce^{4+} and MnO_4^- as titrant, are the subject of study. The transferred particle, the electron, takes the place of $[X]$ in Eq. (22). The numerical values obtained by applying the hyperbolic sine method proposed in this contribution are checked against the method devised by de Levie [62], thus verifying the identity of the results in all cases.

4.1. Fe^{2+} titration curve with Ce^{4+}

The equilibrium constant and pe of the semi-reaction $\text{Ce}^{4+} + e = \text{Ce}^{3+}$ ($E_{0T} = 1.44$ v) are given (Ce^{4+} is the acceptor) by

$$K_T = \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}][e]} \quad pe = \log K_T + \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \quad (28)$$

Also, for the half-reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ ($E_{0S} = 0.68$ v) (Fe^{2+} is the donor)

$$K_S = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}][e]} \quad pe = \log K_S + \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (29)$$

The equilibrium constant of the overall reaction is expressed as

$$\text{Ce}^{4+} + \text{Fe}^{2+} = \text{Ce}^{3+} + \text{Fe}^{3+}, \quad K = \frac{[\text{Ce}^{3+}][\text{Fe}^{3+}]}{[\text{Ce}^{4+}][\text{Fe}^{2+}]} = \frac{K_T}{K_S} \quad (30)$$

From Eq. (22) taking into account that $[X] = e$, and that $a = b = 1$

$$\Delta T = \frac{2\sqrt{K_S/K_T}}{1 + [e]K_S} [e]^{(1-1)/2} \sinh\left(\ln 10(1+1)\left(\frac{pe - pe_{eq}}{2}\right)\right) = \frac{2\sqrt{K_S/K_T}}{1 + 10^{-pe}K_S} \sinh(\ln 10(pe - pe_{eq})) \quad (31)$$

From the Nernst equations applied to the two half-directions involved

$$E = E_T^0 + 0.06 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \quad \frac{E}{0.06} = \frac{E_T^0}{0.06} + \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \quad pe = pe_T^0 + \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \quad (32)$$

$$E = E_S^0 + 0.06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad \frac{E}{0.06} = \frac{E_S^0}{0.06} + \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad pe = pe_S^0 + \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (33)$$

and taking into account Eqs. (28) and (29) are reached

$$pe = \frac{E}{0.06} \quad (34)$$

$$pe_T^0 = \frac{E_T^0}{0.06} = \log K_T \quad \log K_T = \frac{1.44}{0.06} = 24 \quad K_T = 10^{24} \quad (35)$$

$$pe_S^0 = \frac{E_S^0}{0.06} = \log K_S \quad \log K_S = \frac{0.68}{0.06} = 11.333 \quad K_S = 2.154 \cdot 10^{11} \quad (36)$$

The value of pe_{eq} is calculated, Eq. (32), from the expression

$$pe_{eq} = \frac{\log K_T + \log K_S}{a + b} = \frac{24 + 11.333}{1 + 1} = 17.667 \quad (37)$$

whereby the potential at the point of equivalence is given by the expressions

$$E_{eq} = pe_{eq} \cdot 0.06 = 17.667 \cdot 0.06 = 1.06; \quad E_{eq} = \frac{E_T^0 + E_S^0}{2} = \frac{1.44 + 0.68}{2} = 1.06 \quad (38)$$

Note that

$$T = \Delta T + 1 \quad (39)$$

which allows us to calculate the titration curve (**Figure 1**)

$$pe = f(T) \quad E = f(T) \quad (40)$$

or the graph of the titration error (**Figure 2**)

$$\Delta T = f(\Delta pe) \quad \Delta T = f(E) \quad (41)$$

The required calculations are detailed (from 0.62 to 0.82 v) in **Table 1**. Note that when $T = 0.5$, the potential value, $E = 0.68$ v, coincides with the normal potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$. Continuing the calculations would prove that when $T = 2$, $E = 1.44$ v, normal potential value of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ pair.

4.2. Tl^+ titration curve with Ce^{4+}

For the system $\text{Tl}^{3+} + 2e = \text{Tl}^+$ ($E_{0S} = 1.25$ v) the equilibrium constant K_S and pe

$$K_S = \frac{[\text{Tl}^+]}{[\text{Tl}^{3+}][e]^2} \quad pe = \frac{\log K_S}{2} + \frac{1}{2} \log \frac{[\text{Tl}^{3+}]}{[\text{Tl}^+]} \quad (42)$$

Titration of Fe^{2+} with Ce^{4+} (1M H_2SO_4)

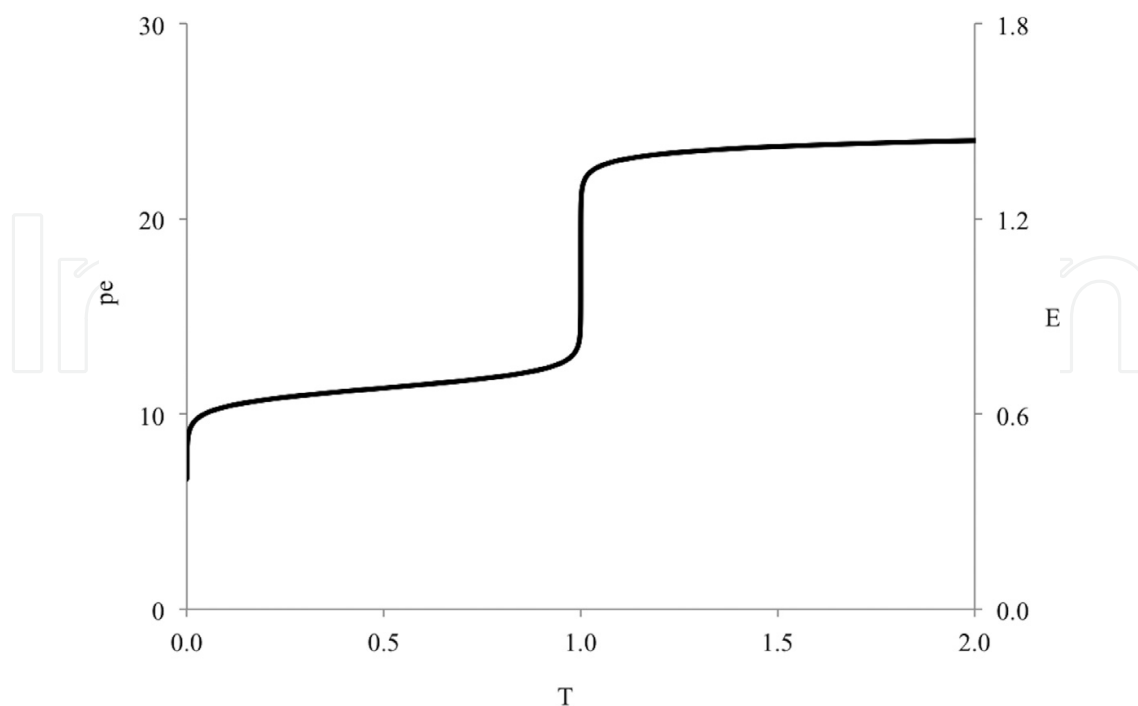


Figure 1. Titration curve of Fe^{2+} with Ce^{4+} in acid medium (H_2SO_4 1 M).

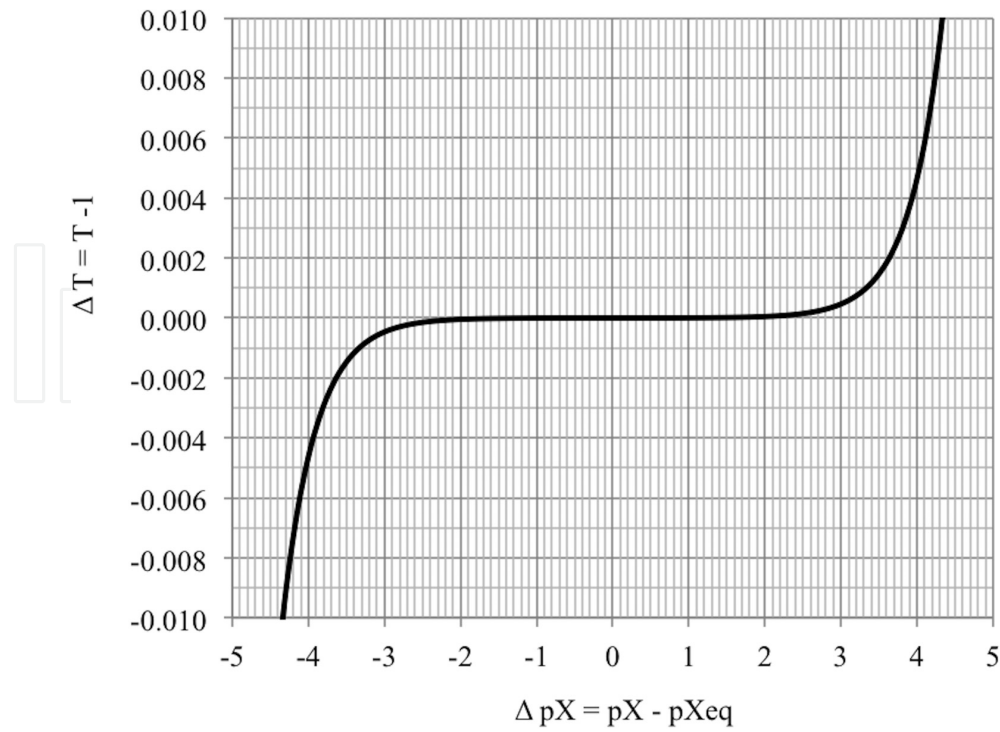
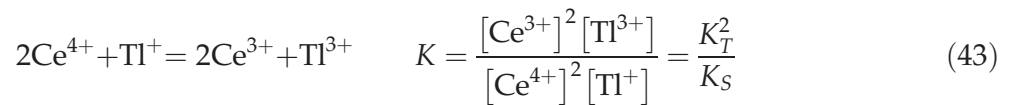


Figure 2. Titration error diagram $\Delta T = f(\Delta pX)$.

The overall reaction and its equilibrium constant are expressed as



Applying the Nernst equation to the half-reaction $\text{Ti}^{3+}/\text{Ti}^{4+}$

$$E = E_S^0 + \frac{0.06}{2} \log \frac{[\text{Ti}^{3+}]}{[\text{Ti}^{4+}]} \quad \frac{E}{0.06} = \frac{E_S^0}{0.06} + \frac{1}{2} \log \frac{[\text{Ti}^{3+}]}{[\text{Ti}^{4+}]} \quad pe = pe_S^0 + \frac{1}{2} \log \frac{[\text{Ti}^{3+}]}{[\text{Ti}^{4+}]} \quad (44)$$

$$pe_S^0 = \frac{E_S^0}{0.06} = \frac{\log K_S}{2} \quad \log K_S = 2 \frac{1.25}{0.06} = 41.666 \quad K_S = 4.642 \cdot 10^{41} \quad (45)$$

$$pe_{eq} = \frac{\log K_T + \log K_S}{a + b} = \frac{24 + 41.666}{1 + 2} = 21.889 \quad (46)$$

$$E_{eq} = pe_{eq} \cdot 0.06 = 21.889 \cdot 0.06 = 1.313; \quad E_{eq} = \frac{E_T^0 + 2E_S^0}{1 + 2} = \frac{1.44 + 21.25}{3} = 1.313 \quad (47)$$

The values of K_S (Eq. 45), K_T (Eq. 35), pe (Eq. 34) and pe_{eq} (Eq. 46) can be replaced in Eq. (22), taking into account that $a = 2$ and $b = 1$

Ce(IV) + Fe(II) = Ce(III) + Fe(III)										
EOT=1.44		neT=1		nHT=0		f(pHT)= 0		pH=-0.3		1M H2SO4
EOS=0.68		neS=1		nHS=0		f(pHS)= 0		EOT'=1.44		
KT'=1.000E+24		KS'=2.154E+11		Wc=9.283E-07		pXeq=17.667		EOS'=0.68		
Ws	[X]^(a-b)/2	W	sine h	ΔT	T	E	X	pX	ΔpX	LOG (ABS(ΔT))
0.091	1	8.439E-08	-1.077E+07	-0.9091	0.0909	0.62	4.642E-11	10.333	-7.333	-0.041
0.128	1	1.188E-07	-7.339E+06	-0.8720	0.1280	0.63	3.162E-11	10.500	-7.167	-0.059
0.177	1	1.645E-07	-5.000E+06	-0.8227	0.1773	0.64	2.154E-11	10.667	-7.000	-0.085
0.240	1	2.230E-07	-3.406E+06	-0.7597	0.2403	0.65	1.468E-11	10.833	-6.833	-0.119
0.317	1	2.943E-07	-2.321E+06	-0.6830	0.3170	0.66	1.000E-11	11.000	-6.667	-0.166
0.405	1	3.762E-07	-1.581E+06	-0.5948	0.4052	0.67	6.813E-12	11.167	-6.500	-0.226
0.500	1	4.642E-07	-1.077E+06	-0.5000	0.5000	0.68	4.642E-12	11.333	-6.333	-0.301
0.595	1	5.521E-07	-7.339E+05	-0.4052	0.5948	0.69	3.162E-12	11.500	-6.167	-0.392
0.683	1	6.340E-07	-5.000E+05	-0.3170	0.6830	0.70	2.154E-12	11.667	-6.000	-0.499
0.760	1	7.053E-07	-3.406E+05	-0.2403	0.7597	0.71	1.468E-12	11.833	-5.833	-0.619
0.823	1	7.638E-07	-2.321E+05	-0.1773	0.8227	0.72	1.000E-12	12.000	-5.667	-0.751
0.872	1	8.095E-07	-1.581E+05	-0.1280	0.8720	0.73	6.813E-13	12.167	-5.500	-0.893
0.909	1	8.439E-07	-1.077E+05	-0.0909	0.9091	0.74	4.642E-13	12.333	-5.333	-1.041
0.936	1	8.691E-07	-7.339E+04	-6.378E-02	0.9362	0.75	3.162E-13	12.500	-5.167	-1.195
0.956	1	8.871E-07	-5.000E+04	-4.436E-02	0.9556	0.76	2.154E-13	12.667	-5.000	-1.353
0.969	1	8.999E-07	-3.406E+04	-3.065E-02	0.9693	0.77	1.468E-13	12.833	-4.833	-1.514
0.979	1	9.087E-07	-2.321E+04	-2.109E-02	0.9789	0.78	1.000E-13	13.000	-4.667	-1.676
0.986	1	9.149E-07	-1.581E+04	-1.447E-02	0.9855	0.79	6.813E-14	13.167	-4.500	-1.840
0.990	1	9.191E-07	-1.077E+04	-9.901E-03	0.9901	0.80	4.642E-14	13.333	-4.333	-2.004
0.993	1	9.220E-07	-7.339E+03	-6.767E-03	0.9932	0.81	3.162E-14	13.500	-4.167	-2.170
0.995	1	9.240E-07	-5.000E+03	-4.620E-03	0.9954	0.82	2.154E-14	13.667	-4.000	-2.335

Table 1. Titration curve of Fe(II) with Ce(IV): hyperbolic sine method.

$$\Delta T = \frac{2\sqrt{K_S/K_T}}{1 + [e]^2 K_S} [e]^{\frac{2-1}{2}} \sinh\left(\ln 10(2+1)\left(\frac{pe - pe_{eq}}{2}\right)\right) \quad (48)$$

$$= \frac{2\sqrt{K_S/K_T}}{1 + 10^{-2pe} K_S} \sqrt{e} \sinh\left(\frac{3}{2} \ln 10(pe - 21.889)\right)$$

The titration curve $E = f(T)$ is shown in **Figure 3**, together with those corresponding to other half-reactions exchanging a single electron, VO^{2+}/VO_2^+ ($E_0 = 1.001\text{ v}$), NO_3^-/NO_2 ($E_0 = 0.80\text{ v}$), and Fe^{3+}/Fe^{2+} ($E_0 = 0.68\text{ v}$).

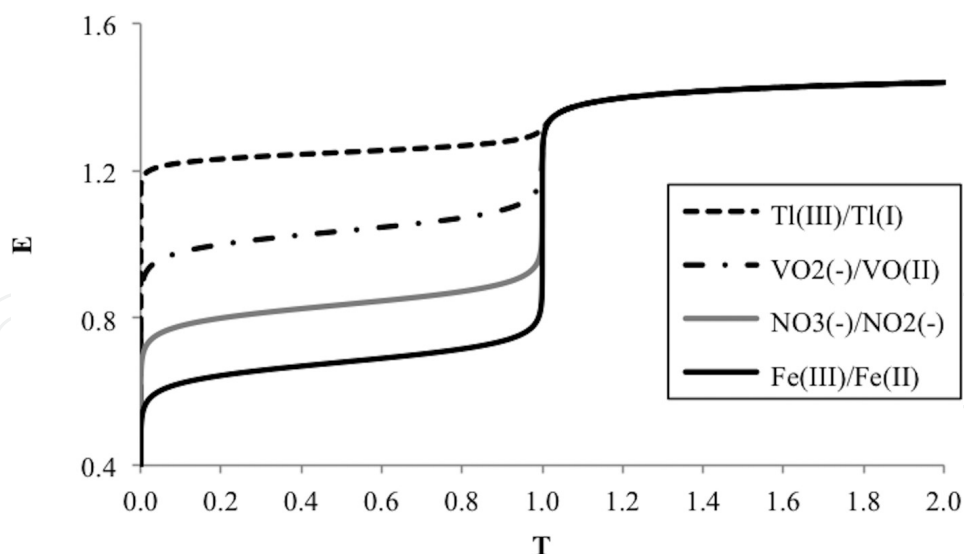


Figure 3. Titration curves of several redox systems with Ce^{4+} as a titrant.

4.3. $\text{Fe}^{2+} + \text{Tl}^+$ titration curve with Ce^{4+}

In this particular case, the total ΔT function (or total T) is additive, i.e., ΔT is the sum of the values of $\Delta T(T)$ corresponding to the individual titration of Fe^{+2} with Ce^{+4} and Tl^+ with Ce^{+4} . The reactions and equations involved have been previously described in Sections 4.1. and 4.2.. Thus, in this case we should only sum the values given by Eqs. 31 (Fe^{+2} with Ce^{+4}) and 48 (Tl^+ with Ce^{+4}). The corresponding titration curve of a mixture of Fe^{2+} and Tl^+ with Ce^{4+} calculated in this way is shown in **Figure 4**.

4.4. Fe^{2+} titration curve with MnO_4^- as titrant

For the half-reaction $\text{MnO}_4^- + 5 e + 8 \text{H}^+ = \text{Mn}^{2+} + 4 \text{H}_2\text{O}$ ($E_{0T} = 1.51 \text{ v}$)

$$K_T = \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][e]^5[\text{H}^+]^8} \quad pe = \frac{\log K_T}{5} - \frac{8}{5}pH + \frac{1}{5}\log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad (49)$$

$$E = E_0^T + \frac{0.06}{5}\log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} = E_0^T - \frac{0.06 \cdot 8}{5}pH + \frac{0.06}{5}\log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad (50)$$

and thus following the previous procedure

$$\frac{E}{0.06} = \frac{E_0^T}{0.06} - \frac{8}{5}pH + \frac{1}{5}\log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad pe = pe_0^T - \frac{8}{5}pH + \frac{1}{5}\log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad (51)$$

$$pe = \frac{E}{0.06} \quad (52)$$

$$pe_0^T = \frac{E_0^T}{0.06} = \frac{\log K_T}{5} \quad \log K_T = 5 \frac{E_0^T}{0.06} \quad K_T = 10^{5 \frac{E_0^T}{0.06}} \quad (53)$$

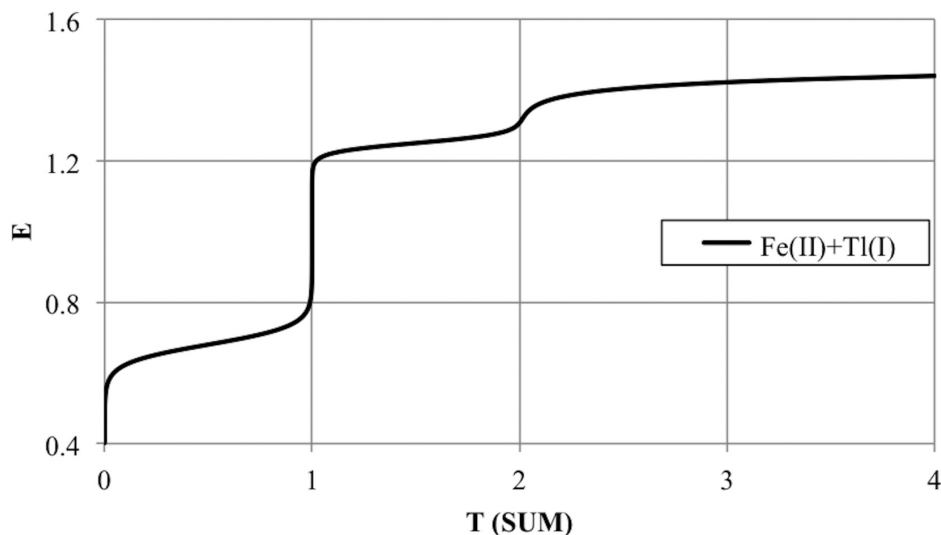


Figure 4. Titration curve of a mixture of Fe^{2+} and Tl^+ with Ce^{4+} .

$$pe_0^{T'} = pe_0^T - \frac{8}{5}pH = \frac{\log K_T}{5} - \frac{8}{5}pH = \frac{\log K'_T}{5} \quad \log K'_T = \log K_T - 8pH \quad (54)$$

The terms of Eq. (54) are conditional (pH -dependent). In the equivalence point

$$pe'_{\text{eq}} = \frac{\log K'_T + \log K'_S}{a + b} \quad (55)$$

The expression for the valuation error will be given by ($a = 1$, $b = 5$)

$$\Delta T = \frac{2\sqrt{K'_S/K'_T}}{1 + [e]K'_S} [e]^{\frac{1-5}{2}} \sinh \left(\ln 10(5 + 1) \left(\frac{\Delta pe}{2} \right) \right) = \frac{2\sqrt{K'_S/K'_T}}{1 + [e]K'_S} [e]^{-2} \sinh(3 \ln 10(pe - pe'_{\text{eq}})) \quad (56)$$

The curve and the titration error are shown in **Figures 5** and **6**, respectively, at different pH values. Part of the necessary calculations, at $pH = 0$, is shown in **Table 2**. When $T = 2$ and $pH = 0$, $E = 1.51$ V, normal $\text{MnO}_4^-/\text{Mn}^{2+}$ system potential.

4.5. Titration curve of V^{2+} with MnO_4^-

Oxido-reductor systems involving the vanadium oxidation states 2+, 3+, 4+, and 5+ are shown in **Table 3**. The V^{2+} ion undergoes various successive ionizations at 3+, 4+, and 5+ when MnO_4^- is added, being appreciated in the curve (**Figure 7**), the three corresponding jumps. The total ΔT function (or total T) is additive. The titration curve is the sum of the contributions of each individual reaction

$$\Delta T_{\text{SUM}} = \Delta T_{32} + \Delta T_{43} + \Delta T_{54} \quad (57)$$

$$T_{\text{SUM}} = \Delta T_{\text{SUM}} - 3 = T_{32} + T_{43} + T_{54} \quad (58)$$

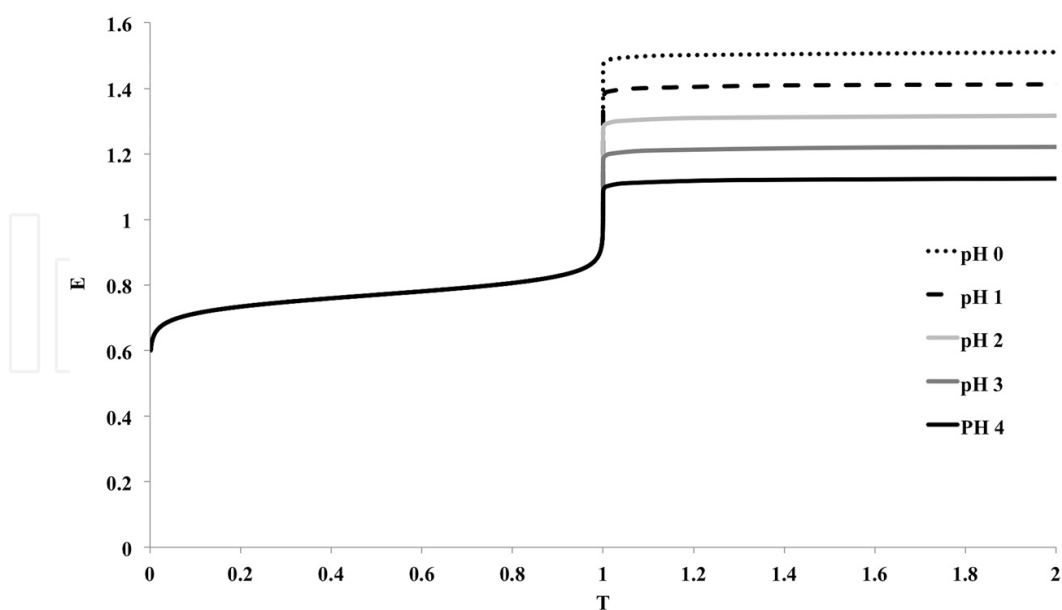


Figure 5. Titration curve of Fe^{2+} with MnO_4^- , at different pH values.

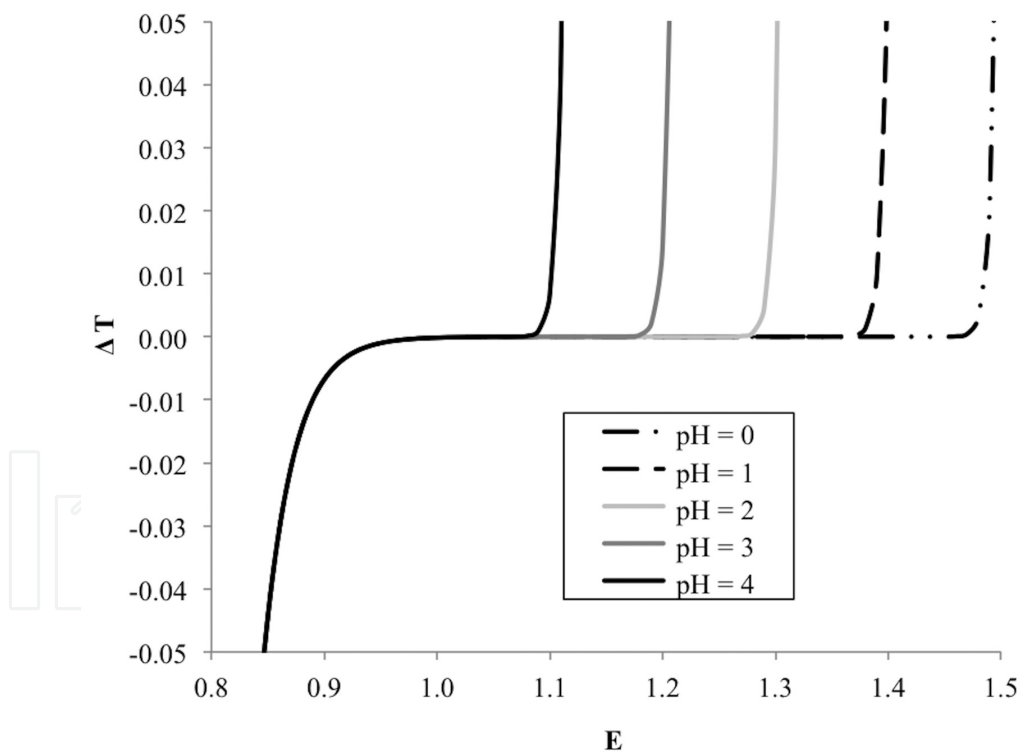


Figure 6. Titration error diagram $\Delta T = f(E)$ at different pH values.

The head of the spreadsheet in EXCEL with all the necessary elements to carry out the numerical calculations applying the equations of the type of Eq. (22) is shown in **Table 3**. From the corresponding EXCEL sheet we have extracted a few columns, those corresponding to the

						$pH=0$		$MnO_4^- + 5 Fe(II) + 8 H^+ = Mn(II) + 5 Fe(III) + 4 H_2O$		
$EOT=1.51$	$neT=5$	$nHT=8$	$f(pHT)=0$	$EOT'=1.51$						
$EOS=0.77$	$neS=1$	$nHS=0$	$f(pHS)=0$	$EOS'=0.77$						
$KT'=6.8129E+125$	$KS'=6.81292E+12$	$Wc=6.32456E-57$	$pXeq=23.111$	$Eeq=1.387$						
Ws	$[X]^{(a-b)/2}$	W	sine h	ΔT	T	E	X	pX	ΔpX	LOG(ABS (ΔpX))
0.0909	4.642E+23	2.669E-34	-3.406E+33	-0.9091	0.0909	0.71	1.468E-12	11.833	-11.278	-4.139E-02
0.1280	1.000E+24	8.095E-34	-1.077E+33	-0.8720	0.1280	0.72	1.000E-12	12.000	-11.111	-5.948E-02
0.1773	2.154E+24	2.415E-33	-3.406E+32	-0.8227	0.1773	0.73	6.813E-13	12.167	-10.944	-8.473E-02
0.2403	4.642E+24	7.053E-33	-1.077E+32	-0.7597	0.2403	0.74	4.642E-13	12.333	-10.778	-1.193E-01
0.3170	1.000E+25	2.005E-32	-3.406E+31	-0.6830	0.3170	0.75	3.162E-13	12.500	-10.611	-1.656E-01
0.4052	2.154E+25	5.521E-32	-1.077E+31	-0.5948	0.4052	0.76	2.154E-13	12.667	-10.444	-2.256E-01
0.5000	4.642E+25	1.468E-31	-3.406E+30	-0.5000	0.5000	0.77	1.468E-13	12.833	-10.278	-3.010E-01
0.5948	1.000E+26	3.762E-31	-1.077E+30	-0.4052	0.5948	0.78	1.000E-13	13.000	-10.111	-3.923E-01
0.6830	2.154E+26	9.306E-31	-3.406E+29	-0.3170	0.6830	0.79	6.813E-14	13.167	-9.944	-4.989E-01
0.7597	4.642E+26	2.230E-30	-1.077E+29	-0.2403	0.7597	0.80	4.642E-14	13.333	-9.778	-6.193E-01
0.8227	1.000E+27	5.203E-30	-3.406E+28	-0.1773	0.8227	0.81	3.162E-14	13.500	-9.611	-7.514E-01
0.8720	2.154E+27	1.188E-29	-1.077E+28	-0.1280	0.8720	0.82	2.154E-14	13.667	-9.444	-8.928E-01
0.9091	4.642E+27	2.669E-29	-3.406E+27	-0.0909	0.9091	0.83	1.468E-14	13.833	-9.278	-1.041E+00
0.9362	1.000E+28	5.921E-29	-1.077E+27	-0.0638	0.9362	0.84	1.000E-14	14.000	-9.111	-1.195E+00
0.9556	2.154E+28	1.302E-28	-3.406E+26	-0.0444	0.9556	0.85	6.813E-15	14.167	-8.944	-1.353E+00
0.9693	4.642E+28	2.846E-28	-1.077E+26	-0.0307	0.9693	0.86	4.642E-15	14.333	-8.778	-1.514E+00
0.9789	1.000E+29	6.191E-28	-3.406E+25	-0.0211	0.9789	0.87	3.162E-15	14.500	-8.611	-1.676E+00
0.9855	2.154E+29	1.343E-27	-1.077E+25	-0.0145	0.9855	0.88	2.154E-15	14.667	-8.444	-1.840E+00
0.9901	4.642E+29	2.907E-27	-3.406E+24	-0.0099	0.9901	0.89	1.468E-15	14.833	-8.278	-2.004E+00
0.9932	1.000E+30	6.282E-27	-1.077E+24	-0.0068	0.9932	0.90	1.000E-15	15.000	-8.111	-2.170E+00
0.9954	2.154E+30	1.356E-26	-3.406E+23	-0.0046	0.9954	0.91	6.813E-16	15.167	-7.944	-2.335E+00

Table 2. Titration curve of Fe(II) with MnO₄(-).

values of E , pX , $T1$, $T2$, $T3$ and T_{SUM} (1, 2, 3 refer to 32, 43, and 54, respectively, in Eqs. 57 and 58, that is, the oxidations of V^{2+} to V^{3+} , from this to VO^{2+} and from this to VO_2^+), which are shown in **Table 4**.

Potential values varying from 0.05 in 0.05 units have been varied in this table in order to cover the entire valuation curve. **Figure 7** has been drawn instead with potential variations of only 0.01 v.

EOT		$MnO_4^- + 8 H^+ + 5e = Mn(II) + 4 H_2O$		
$E032$		$V(III) + e = V(II)$		
$E043$		$VO(II) + 2 H^+ + e = V(III) + H_2O$		
$E054$		$VO_2(I) + 2 H^+ + e = VO(II) + H_2O$		
		$pH=0$		
$EOT=1.51$	$neT=5$	$nHT=8$	$f(pHT)=0$	$EOT'=1.51$
$E0S32=-0.255$	$neS32=1$	$nHS32=0$	$f(pHS32)=0$	$E0S32'=-0.255$
$E0S43=0.337$	$neS43=1$	$nHS43=2$	$f(pHS43)=0$	$E0S43'=0.337$
$E0S54=1.001$	$neS54=1$	$nH54=2$	$f(pH54)=0$	$E0S54'=1.001$
$KT=6.813E+125$				
$KS32'=5.623E-05$	$Wc32=1.817E-65$	$pXeq1=20.264$		
$KS43'=4.137E+05$	$Wc43=1.558E-60$	$pXeq2=21.908$		
$KS54'=4.82318E+16$	$Wc54=5.321E-55$	$pXeq3=23.753$		

Table 3. Head of the spreadsheet in EXCEL of the titration curve of V(II) with MnO4-.

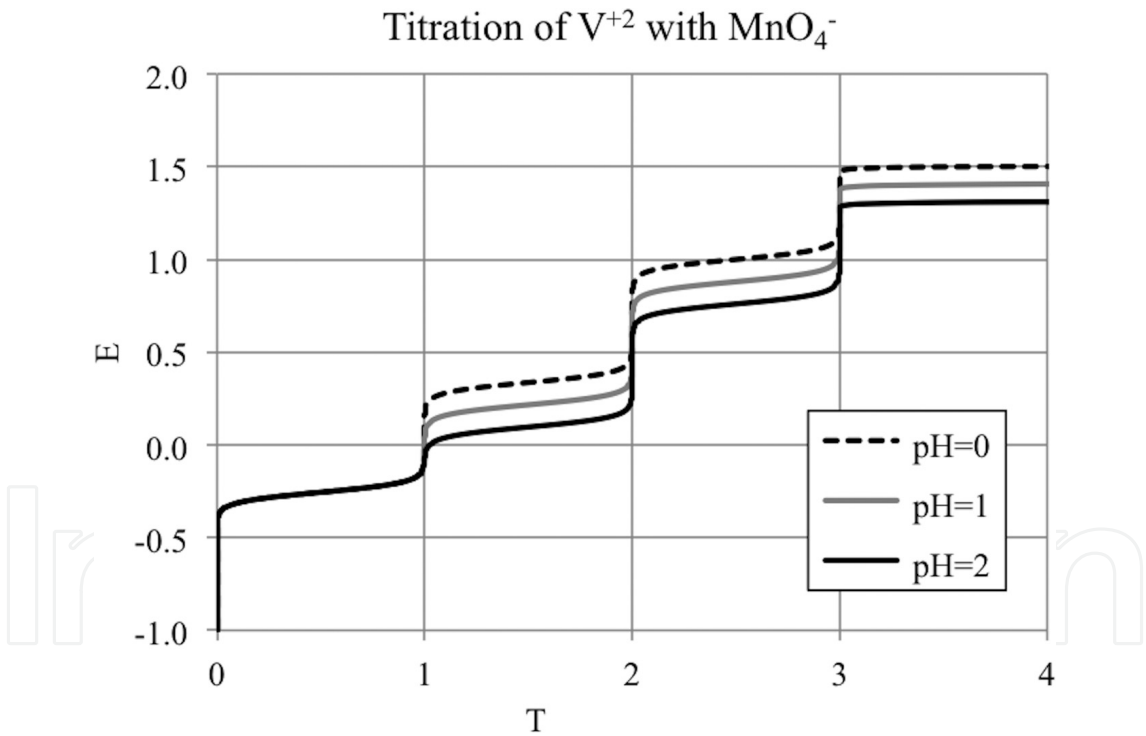


Figure 7. Titration curve of V²⁺ with MnO₄⁻, at pH 0, 1 and 2.

5. Criterion for the quantitative titration and the influence of side-reactions

The principle of redox titrations is that the solution of a reducing agent is titrated with a solution of an oxidizing agent (or vice versa)

<i>T</i> 1	<i>T</i> 2	<i>T</i> 3	<i>T</i> SUM	<i>E</i>	<i>pX</i>
0.0001	0	0	0.0001	−0.5	−8.333
0.0006	0	0	0.0006	−0.45	−7.5
0.0038	0	0	0.0038	−0.4	−6.667
0.0254	0	0	0.0254	−0.35	−5.833
0.151	0	0	0.151	−0.3	−5
0.5478	0	0	0.5478	−0.25	−4.167
0.8919	0	0	0.8919	−0.2	−3.333
0.9825	0	0	0.9825	−0.15	−2.5
0.9974	0	0	0.9974	−0.1	−1.667
0.9996	0	0	0.9996	−0.05	−0.833
0.9999	0	0	0.9999	0	0
1	0	0	1	0.05	0.833
1	0.0001	0	1.0001	0.1	1.667
1	0.0008	0	1.0008	0.15	2.5
1	0.0052	0	1.0052	0.2	3.333
1	0.0343	0	1.0343	0.25	4.167
1	0.1947	0	1.1947	0.3	5
1	0.6222	0	1.6222	0.35	5.833
1	0.9182	0	1.9182	0.4	6.667
1	0.9871	0	1.9871	0.45	7.5
1	0.9981	0	1.9981	0.5	8.333
1	0.9997	0	1.9997	0.55	9.167
1	1	0	2	0.6	10
1	1	0	2	0.65	10.833
1	1	0	2	0.7	11.667
1	1	0.0001	2.0001	0.75	12.5
1	1	0.0004	2.0004	0.8	13.333
1	1	0.003	2.003	0.85	14.167
1	1	0.0203	2.0203	0.9	15
1	1	0.1238	2.1238	0.95	15.833
1	1	0.4904	2.4904	1	16.667
1	1	0.8677	2.8677	1.05	17.5
1	1	0.9781	2.9781	1.1	18.333
1	1	0.9967	2.9967	1.15	19.167
1	1	0.9995	2.9995	1.2	20
1	1	0.9999	2.9999	1.25	20.833

<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 .

The criterion for the feasibility of the titration, according to Eq. (64) is:

$$2\log K'_{\text{Fe}(\text{CN})_6} - \log K'_A > 3(1 + 2) = 9 \quad (69)$$

From the protonation constants of hexacyanoferrate(II), if the $pH > 5.5$, then $\alpha_{\text{Fe}(\text{CN})_6(\text{H})} = 1$ and

$$\log K'_{\text{Fe}(\text{CN})_6} = \log K_{\text{Fe}(\text{CN})_6} = 6.1. \quad (70)$$

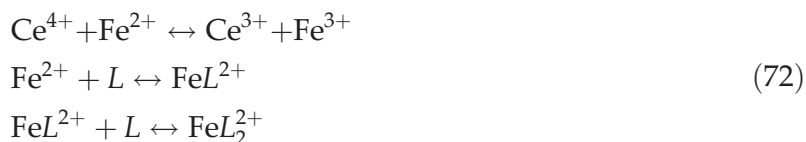
Therefore $2 \times 6.1 - \log K'_A > 9$; or $\log K'_A < 3.2$. If the $pH = 6$, then $\alpha_{A(\text{H})} = 1 + 10^{-6} \times 10^{11.57} + 10^{-12} \times 10^{15.73} = 10^{5.58}$

$$\log K'_A = 3.1 \quad (71)$$

Thus, if the $pH > 6$, the titration can be performed with adequate accuracy.

(2) Calculate the $[L]$ maximum for the accurate direct titration of Ce^{+4} with Fe^{2+} , being L the organic complexant (acetylacetone) present in the solution and given that $\log K_T = 24$ and $\log K_S = 11.3$ (see Eqs. (28)–(30)); the global constants of $\text{Fe}(\text{L})(\text{II})$ are $\log \beta_1 = 5.07$; $\log \beta_2 = 8.67$.

The reactions involved would be



The criterion for the feasibility of the titration, according to Eq. (64) is

$$\log K_T - \log K'_S > 3(1 + 1) = 6 \quad (73)$$

$$\log K_T - 6 > \log K'_S, \quad \log K'_S < 18 \quad (74)$$

$$\begin{aligned} K'_S &= K_S \alpha_{[\text{FeL}_2]^{+2}}, \quad \alpha_{[\text{FeL}_2]^{+2}} < 10^{6.7} \\ \alpha_{[\text{FeL}_2]^{+2}} &= 1 + [L]\beta_1 + [L]^2\beta_2 \end{aligned} \quad (75)$$

Thus, if the $[L] < 0.1 \text{ M}$, the titration can be performed with adequate accuracy.

(3) Calculate the $[\text{SO}_4^{-2}]$ maximum present in the solution for the accurate direct titration of Ce^{4+} with Ti^{+} , given that $\log K_T = 24$ and $\log K_S = 41.6$ (see Eqs. (28), (42), (43)); the global constants of $\text{Ce}(\text{SO}_4)(\text{IV})$ are $\log \beta_1 = 3.5$; $\log \beta_2 = 8.0$; $\log \beta_3 = 10.4$.

The criterion for the feasibility of the titration, according to (64) is:

$$2\log K'_T - \log K_S > 3(1 + 2) = 9 \quad (76)$$

$$\log K'_T > 25.3$$

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

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

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., $\text{Fe(II)} + \text{Ti(I)}$, 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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