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The Simulation of an Oxidation–Reduction Titration Curve with Computer Algebra

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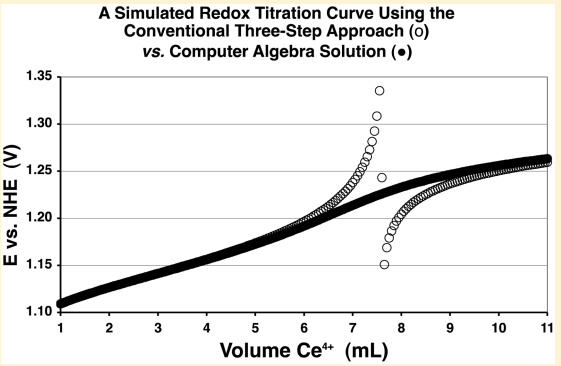
Supporting Information

ABSTRACT: Although the simulation of an oxidation/reduction titration curve is an important exercise in an undergraduate course in quantitative analysis, that exercise is frequently simplified to accommodate computational limitations. With the use of readily available computer algebra systems, however, such curves for complicated systems can be generated from a single expression for the mixed potential of the solution. A single-expression approach broadens the scope of reactions that can be simulated, and it demonstrates the effects of the completeness of the titration near the equivalence point. The titration of Br^{1-} with Ce(IV) is given as an example and compared to the classic method of simulating the titration curve.



KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Computer-Based Learning, Oxidation/Reduction, Titration/Volumetric Analysis*

INTRODUCTION

The simulation of a potentiometric titration curve for a redox titration is an important exercise in the beginning course in quantitative analysis. It allows the student to see the proximity of the equivalence point to a significant potential change and the factors that have an effect on that change. If we consider the titration of an oxidizable agent R_2 with an oxidizing agent Ox_1 such that

$$Ox_1 + n_1e^- \rightleftharpoons R_1 \quad \text{with } E^\circ_1 \tag{1}$$

$$Ox_2 + n_2e^- \rightleftharpoons R_2 \quad \text{with } E^\circ_2 \tag{2}$$

the stoichiometry for the titration becomes

$$n_2Ox_1 + n_1R_2 \rightleftharpoons n_1Ox_2 + n_2R_1 \tag{3}$$

The standard procedure for the simulation becomes a three-part problem: First, the potential of the indicator electrode prior to the equivalence point is calculated from the Nernst equation using only the redox couple for the titrand. That would be

$$E = E^\circ_2 - \frac{RT}{n_2F}\ln\frac{[R_2]}{[Ox_2]} \tag{4}$$

Second, at the equivalence point, the potential is found from the mixed potential of the standard reduction potentials:

$$E = \frac{n_1E^\circ_1 + n_2E^\circ_2}{n_1 + n_2} - \frac{RT}{(n_1 + n_2)F}\ln\frac{[R_1][R_2]}{[Ox_1][Ox_2]} \tag{5}$$

And third, after the equivalence point, one works from the concentrations of the titrant's reactant and product. That is

$$E = E^\circ_1 - \frac{RT}{n_1F}\ln\frac{[R_1]}{[Ox_1]} \tag{6}$$

Integration of these three steps creates a classic titration plot, but the exercise is misleading on two counts: it presumes, without warning, that the equilibrium of eq 3 lies far, far to the right, which is true *only* when $E^\circ_1 - E^\circ_2$ ($=\Delta E^\circ$) is large. And second, the equivalence point potential is typically (always) calculated from a simplified form of eq 5, a form which does not contain the log term. But that log term can be dropped (set equal to zero) only when the coefficient for Ox_1 equals the coefficient for R_1 and the coefficient for R_2 equals the coefficient for Ox_2 in eqs 1 and 2, respectively. This restriction is rarely pointed out although it is severe because it precludes the study of redox titrations involving $[H^+]$ or polyatomic agents where those coefficients will not allow one to omit the log term.

Both of these issues are resolved when the potential is determined throughout the titration, purely as a mixed potential; that is, by using the complete eq 5 throughout the titration. Doing so requires the solution of up to an $n_1 + n_2$ order polynomial[1] from the equilibrium expression in order to find $[Ox_1]$, $[R_1]$, $[Ox_2]$, and $[R_2]$. Solving such a polynomial, by the way, does not preclude the use of a spreadsheet to generate the titration curve; generating titration curves on a spreadsheet from the solution of polynomials is feasible.[2] And while clever solutions have been offered to alleviate the sometimes difficult spreadsheet calculations,[1,3,4] these can be rendered unnecessary

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by directly simulating the titration curve with computer algebra. Software such as Maple, Mathematica, and Matlab along with open source software like Sage and Python is widely available, and student proficiency with these tools has reached the point that computer algebra is a legitimate approach to solving these problems. The simulation provided here can be extended to convert concentrations to activities by inserting a loop to calculate and apply activity coefficients.[5] But for the sake of clarity, and because it is an unlikely undergraduate assignment, this exercise is deferred to the end of this paper.

The example redox titration curve simulation provided here is an exercise that illustrates the shortcomings of the three-part approach. And while it is presented with computer algebra, specifically Maple, it does not attempt to show that a spreadsheet approach cannot succeed. The Maple worksheet is provided in the Supporting Information.

EXAMPLE

Consider the titration of 10.00 mL of 0.0285 M Br^- with 0.0250 M Ce^{4+} in 1 M H_2SO_4. The stoichiometry would be

$$2Ce^{4+} + 3Br^- \rightleftharpoons Br_3^- + 2Ce^{3+} \tag{7}$$

We are given from Standard Reduction Tables:

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^\circ_{Ce^{4+}} = 1.44\ V \tag{8}$$

$$Br_3^- + 2e^- \rightleftharpoons 3Br^- \qquad E^\circ_{Br3^-} = 1.05\ V \tag{9}$$

The potential at any point during the titration is the mixed potential of the two couples

$$E = \left(E^\circ_{Ce4+} + 2E^\circ_{Br3} - \frac{RT}{F}\ln\frac{[Ce^{3+}][Br^-]^3}{[Ce^{4+}][Br_3^-]}\right)\Big/(1+2) \tag{10}$$

The concentrations in log term in eq 10 require the use of the equilibrium expression for the reaction expressed in 7. This would be

$$K_{eq} = \frac{[Ce^{3+}]^2[Br_3^-]}{[Ce^{4+}]^2[Br^-]^3} \tag{11}$$

where K_{eq} is obtained from

$$E^\circ_{Ce^{4+}} - E^\circ_{Br_3^-} = \frac{RT}{2F}\ln(K_{eq}) \tag{12}$$

The four concentrations are found by using the common "ICE" table technique.[6] First, some nomenclature: C°_{Ce} represents the initial molarity of the Ce^{4+} titrant and C°_{Br} represents the initial molarity of the Br^- titrand. Therefore,

$$C_{Ce} = \frac{V_{Ce}C^\circ_{Ce}}{V_{Ce} + V_{Br}} \tag{13}$$

and

$$C_{Br} = \frac{V_{Br}C^\circ_{Br}}{V_{Ce} + V_{Br}} \tag{14}$$

where C_{Br} and C_{Ce} represent respective analytical concentrations of the titrand, $C_{(Br^{3-},Br^-)}$, and titrant $C_{(Ce^{4+},Ce^{3+})}$, during the titration. These concentrations can be calculated from the given volume of titrand, V_{Br} and the volume of titrant dispensed, V_{Ce}, at any point during[7] the titration. These analytical concentrations also represent individual species' concentrations.

$$C_{Ce} = [Ce^{3+}] + [Ce^{4+}] \tag{15}$$

$$C_{Br} = [Br^-] + 3[Br_3^-] \tag{16}$$

From eq 7 we can write

$$[Br_3^-] = x \tag{17}$$

$$[Br^{1-}] = C_{Br} - 3x \tag{18}$$

$$[Ce^{3+}] = 2x \tag{19}$$

$$[Ce^{4+}] = C_{Ce} - 2x \tag{20}$$

and combining eqs 17−20, eq 11 takes the form

$$K_{eq} = \frac{(2x)^2(x)}{(C_{Ce} - 2x)^2(C_{Br} - 3x)^3} \tag{21}$$

which renders a fifth degree $(n_1 + n_2)$ polynomial. It can be solved with Maple to yield all of its five roots.[8] In the example given here, selection of the only (physically) legitimate root is not entirely trivial. Two of the roots are complex numbers and one of the roots gives an x that yields $[Br^-]$ less than zero; these are readily disqualified. But the remaining two roots produce apparently reasonable values for the four species; however, one of these can be eliminated because it begins to produce complex roots near the equivalence point. With x determined for each incremental volume of Ce^{4+} titrant, the four concentrations necessary for eq 10 can be determined using eqs 17−20, and so E, the potential of the indicator electrode, is determined for every point.

The worksheet in the Supporting Information provides the calculation of the indicator electrode potential from 0.05 mL of Ce^{4+} to 11.00 mL in 0.05 mL increments (220 points). Figure 1[9] illustrates those results, in addition to results for this titration

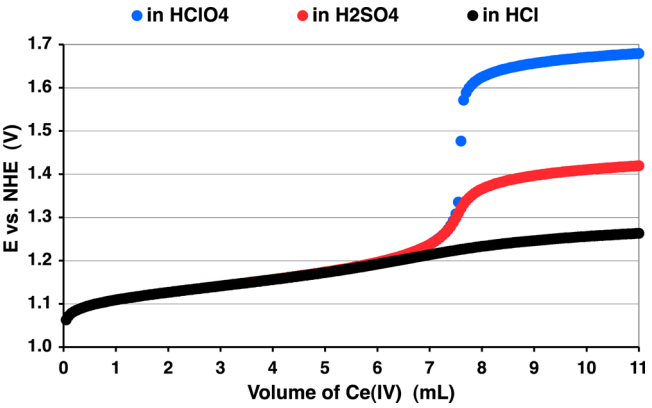

Figure 1. Simulated titration curves for the titration of 10.00 mL of 0.0285 M Br^- solution with 0.0250 M Ce(IV) in 1.0 M solutions of three acids.

with Ce^{4+} in 1 M $HClO_4$ and in 1 M HCl where the $E^\circ_{Ce^{4+}}$ is 1.70 and 1.28 V, respectively. This is to illustrate the importance of an adequate difference between the reduction potentials of the titrant and titrand (ΔE°).

Figure 2 illustrates the results of calculating the same titration curves using the three-part process described above but with one necessary deviation: inasmuch as the three-part algorithm cannot yield an equivalence point potential for this stoichiometry, that point was found by interpolating the

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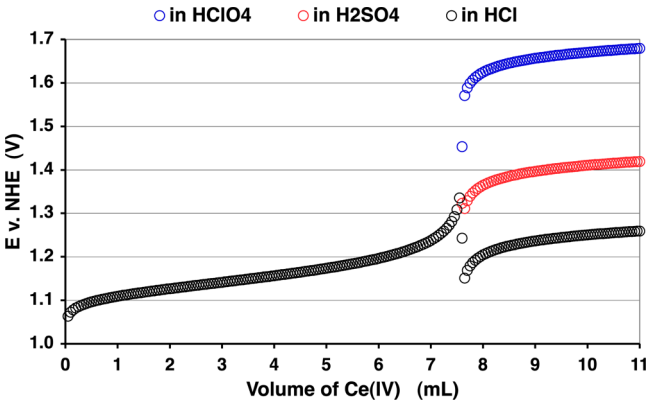

Figure 2. Simulated titration curves for the titration of 10.00 mL of 0.0285 M Br^- solution with 0.0250 M Ce(IV) in 1.0 M solutions of three acids using the conventional three-step calculation.

potential 0.05 mL prior to and 0.05 mL beyond the equivalence point.

The equivalence point lies at 7.60 mL of the Ce(IV) titrant where both approaches show a "break." For the titration in 1 M $HClO_4$, Figures 1 and 2 are similar throughout. But the three-part algorithm must (incorrectly) show identical potentials at every point prior to the equivalence point in all three acids because every point is found using only $[Br^-]^3/[Br_3^-]$, and because it presumes that the equilibrium of eq 7 lies entirely to the right,[10] the curve preceding the equivalence will have an exaggerated slope. The presumption that the bromide is completely oxidized is virtually true where ΔE° is large, but it leads to the inexplicable results for the titration in 1 M HCl where ΔE° is not large.

The titrations in H_2SO_4 and HCl are more closely examined in Figure 3. Apparently the ΔE° (= 1.44−1.05) V for the

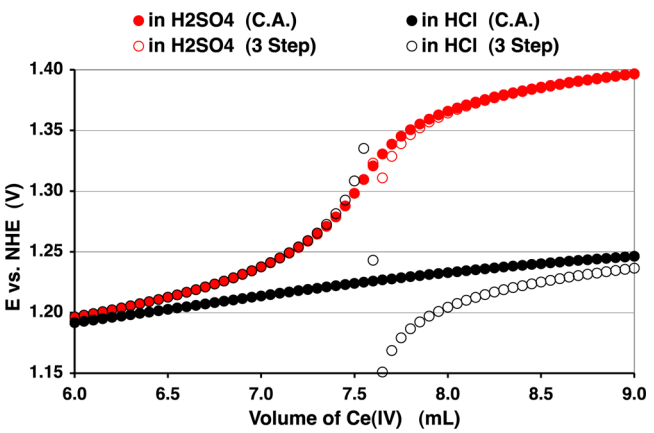

Figure 3. An expansion of the simulated titration curves for the titration of 10.00 mL of 0.0285 M Br^- solution with 0.0250 M Ce(IV) in two of the 1.0 M acid solutions comparing the results from a computer algebra calculation to those from the three-step process.

titration in H_2SO_4 is just large enough to render a good approximation of the titration curve using the three-step process, but this simulation in HCl is inadequate as those results make no sense: the potential appears to change direction just before the equivalence point! Finally, the nearly correct evaluation of E at the equivalence point using the three-part approach is purely serendipitous in that it is the average of two unlikely E's.

While creating plots using computer algebra to calculate mixed potentials throughout the titration affords a superior simulation of such plots, there remains room for improvement: all calculations shown here are based on concentrations rather than activities. It is not difficult to insert (nest) a loop within the program which will calculate the ionic strength at every point in the titration. And from this, calculate the activity of every species in the reaction.[5,11] The effect of this correction is illustrated in Figure 4.

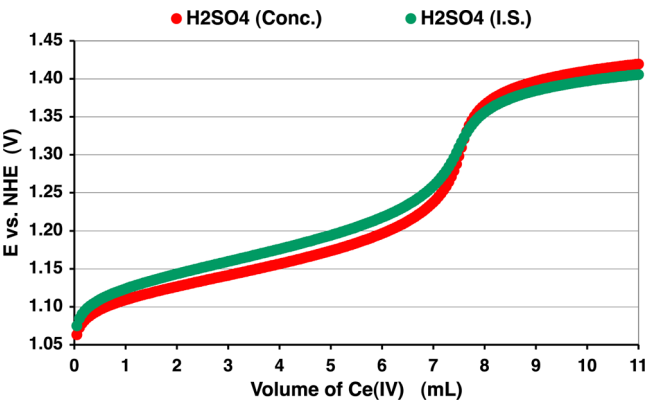

Figure 4. Simulated titration curves for the titration of 10.00 mL of 0.0285 M Br^- solution with 0.0250 M Ce(IV) in 1.0 M H_2SO_4 illustrating the effect of including ionic strength in the calculations.

It would appear that in this case the use of concentrations to calculate the potential at each point exaggerates the "break" near the equivalence point. Here the differences are nearly large enough to change the characterization from adequate (for end point detection) to inadequate. A closer look at the results, however, reveals another measurable error. The inflection point of the titration plot will not coincide with the equivalence point unless the number of electrons exchanged in each half reaction, n_1 and n_2, are equal.[12] The location of the inflection point is especially important when the titration is to be monitored as a differential potential (e.g., with polarized electrodes). That inflection point can be extracted from the calculations of mixed potentials by finding the maximum $^{\Delta E}/_{\Delta V}$ where $\Delta E_i = E_{i+1} - E_{i-1}$ and $\Delta V_i = V_{i+1} - V_{i-1}$. When these differentials are plotted (Figure 5) for concentration-based vs activity-based calcula-

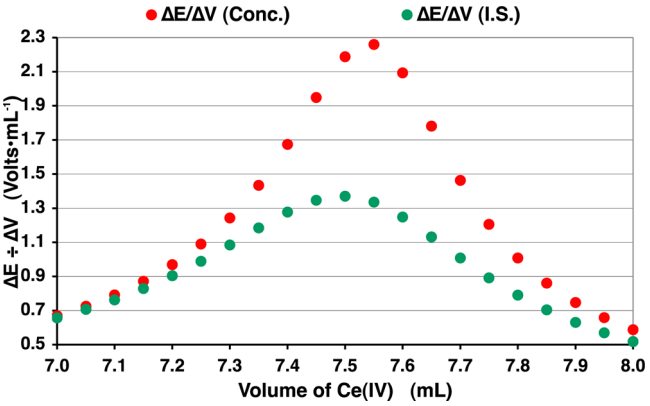

Figure 5. Differential titration curves for the titration of 10.00 mL of 0.0285 M Br^- solution with 0.0250 M Ce(IV) in 1.0 M H_2SO_4 using only concentrations and then correcting with ionic activities to calculate E.

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tions, the results reveal a measurable difference in the location of the inflection points. If the inflection point is taken as the equivalence point, one would infer an equivalence point 0.05 mL premature, when, more correctly, it would be 0.10 mL premature.

CONCLUSION

The simulation of a potentiometric titration curve for a redox titration by calculating every point as a mixed potential can be achieved with computer algebra. The process yields plots of high fidelity and without the discontinuities found in plots derived from the commonly used three-part algorithm. These plots can clearly illustrate the importance of a significant difference in the reduction potentials of the titrant and titrand. The results can be further analyzed to locate the inflection point on the titration curve, and the calculations can be adjusted to address ionic strength effects throughout the titration.

ASSOCIATED CONTENT

Supporting Information

The Maple worksheet used to provide the output for Figures 1−3 has been provided. It contains the algorithm for calculating the three titration curves. It also contains the algorithm one might use for the conventional three-step approach to generating these curves. The worksheet has been shown to run on Maple 13 through 18. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(6) Larsen, D. http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier's_Principle/Ice_Tables (accessed Feb 2015).

(7) "During" implies that $V_{titrant} = 0$ is *not* included, and so an initial volume of Ce^{4+} must be greater than zero.

(8) Maple offers an fsolve command that yields only real roots. This precludes all complex roots, but it has been found to miss some of the real roots without warning.

(9) While Maple graphics provide a good articulation of results, the output does not meet ACS standards for publication, and so the figures presented here have been enhanced by exporting Maple results to an Excel worksheet from which the figures are rendered.

(10) As part of the three-step process, Kropotov has addressed the problem of equilibration that does not lie far toward the products. Kropotov, V. A. Approximation of Redox Titration Curves by Logarithmic Functions. *J. Anal. Chem.* **1998**, *53* (8), 701−703.

(11) The Davies Equation can be used to calculate each activity coefficient. For this, the ionic parameters reported in Kielland, J. Approximation of Activity Coefficients of Ions in Aqueous Solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675−1678 are used. The value for Br_3^- is estimated to be 3.5.

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