Supplementary Topics
for

Quantitative Chemical Analysis

Sixth Edition

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*Note: Figure references with chapter assignments refer to *Quantitative Chemical Analysis* 6e by Dan Harris.

Spreadsheet for Precipitation Titration of a Mixture

We now derive an equation for the shape of the titration curve for a mixture (initial volume = V^o) of the anions X^- (initial concentration = C_X^o) and Y^- (initial concentration = C_Y^o) titrated with M^+ (initial concentration = C_M^o , volume added = V_M) to precipitate MX(s) and MY(s), whose solubility products are K_{sp}^X and K_{sp}^Y . The three mass balances are

Mass balance for M: $C_M^o \cdot V_M = [M^+](V_M + V^o) + \text{mol MX(s)} + \text{mol MY(s)}$ (1)

Mass balance for X: $C_X^o \cdot V^o = [X^-](V_M + V^o) + \text{mol MX(s)}$ (2)

Mass balance for Y: $C_Y^o \cdot V^o = [Y^-](V_M + V^o) + \text{mol MY(s)}$ (3)

Equation 2 can be solved for mol MX(s), and Equation 3 can be solved for mol MY(s). When these two expressions are substituted into Equation 1, we can solve for V_M to find

Precipitation of X^- + Y^- with M^+: $$V_M = V^o\left(\frac{C_X^o + C_Y^o + [M^+] - [X^-] - [Y^-]}{C_M^o - [M^+] + [X^-] + [Y^-]}\right) \qquad (4)$$

The IF Statement

Equation 4 allows us to compute the titration curve for a mixture, but we must be aware of some tricky subtleties. For the first part of the titration of a mixture of I^- and Cl^-, only I^- is precipitating. In this region, we can say $[I^-] = K_{sp}^{AgI}/[Ag^+]$. $[Cl^-]$ is just the initial concentration corrected for dilution ($[Cl^-] = C_{Cl}^o \cdot \{V^o/(V_M + V^o)\}$), because precipitation of AgCl has not commenced. This is the value computed in column D of the spreadsheet in Figure 1. Precipitation of Cl^- begins shortly before the first equivalence point when the product $[Ag^+][Cl^-]$ exceeds K_{sp}^{AgCl} .

$[Cl^-]$ in Equation 4 must therefore be computed with an IF statement:

IF $[Ag^+] < K_{sp}^{AgCl}/[Cl^-]$

then $[Cl^-] = C_{Cl}^o \cdot \{V^o/(V_M + V^o)\}$

otherwise $[Cl^-] = K_{sp}^{AgCl}/[Ag^+]$

A common syntax for testing a logical condition is

IF(logic_statement, value_if_true, value_if_false)

This expression means that if logic_statement is true, value_if_true is returned.

Otherwise, value_if_false is returned. For example, IF(C2>$A$6, 0.05, 0) returns a value of 0.05 if C2>$A$6 and a value of 0 if C2≤$A$6. For the titration of I^- and Cl^-, $[Cl^-]$ in cell E4 in

	A	B	C	D	E	F	G
1	Titration of I- + Cl- by Ag+						
2				[Cl-]			
3	Ksp(AgCl)=	pAg	[Ag+]	Diluted Value	[Cl-]	[I-]	Vm
4	1.80E-10	14.5	3.16E-15	0.0411	4.11E-02	2.62E-02	8.651
5	Ksp(AgI)=	14	1.00E-14	0.0344	3.44E-02	8.30E-03	18.060
6	8.30E-17	13	1.00E-13	0.0317	3.17E-02	8.30E-04	23.143
7	Vo=	12	1.00E-12	0.0314	3.14E-02	8.30E-05	23.701
8	40	11	1.00E-11	0.0314	3.14E-02	8.30E-06	23.757
9	Co(Cl)=	10	1.00E-10	0.0314	3.14E-02	8.30E-07	23.763
10	0.05	9	1.00E-09	0.0314	3.14E-02	8.30E-08	23.763
11	Co(I)=	8	1.00E-08	0.0277	1.80E-02	8.30E-09	32.078
12	0.0502	7	1.00E-07	0.0234	1.80E-03	8.30E-10	45.608
13	Co(Ag)=	6	1.00E-06	0.0229	1.80E-04	8.30E-11	47.247
14	0.0845	5	1.00E-05	0.0229	1.80E-05	8.30E-12	47.424
15		4	1.00E-04	0.0228	1.80E-06	8.30E-13	47.534
16		3	1.00E-03	0.0226	1.80E-07	8.30E-14	48.479
17		2	1.00E-02	0.0202	1.80E-08	8.30E-15	59.168
18							
19	C4 = 10^-B4						
20	D4 = $A$10*($A$8/($A$8+G4))						
21	E4 = If((D4<($A$4/C4)),D4,$A$4/C4)						
22	F4 = $A$6/C4						
23	G2 = $A$8*($A$10+$A$12+C4-E4-F4)/($A$14-C4+E4+F4)						

Figure 1. Spreadsheet for titration of a mixture

the spreadsheet in Figure 1 is calculated with the statement

$$\mathrm{IF}\ ([Cl^-]_{diluted} < K_{sp}^{AgCl}/[Ag^+],\ [Cl^-]_{diluted},\ K_{sp}^{AgCl}/[Ag^+]$$

If ((D4 < ($A$4/C4)), D4, $A$4/C4)

In column D of the spreadsheet in Figure 1 we calculate the concentration of Cl^- on basis of the dilution from the initial volume V^o to the final volume $V_M + V^o$. In column E we calculate the concentration of Cl^- with the IF statement that checks to see whether or not AgCl has precipitated.

There is a very significant subtlety in the spreadsheet in Figure 1. Column D requires the value in column G. But column G requires the value in column E, which uses the value in column D. This is called a *circular definition*. Most spreadsheets allow you to do this and may question you to see if it is really what you meant to do. The first time the value in cell D4 is computed, there is no value in cell G4, so G4=0 is used in cell D4. Then cells E4 and G4 are computed with the value in cell D4. You will need to follow instructions for your spreadsheet to carry out several iterations to reach self-consistent values in columns D through G.

Here is an example of how to get a spreadsheet to accept the circular definition. Unless you have the same spreadsheet that I do, your procedure is probably going to be different and you will need to consult your manual for help. After typing in formulas for the spreadsheet in Figure 1 in Excel 5 on the Macintosh or Excel 7 on a PC, the values in cells D4 through G4 are

Diluted Value	[Cl-]	[I-]	Vm
0.05	0.05	0.0262469	0

Now go to the **Tools** menu and select **Options**. In the window that opens, select **Calculations**. In the **Calculations** window, activate **Iteration** by clicking it. When you close this window the computer begins to carry out successive approximations to resolve the circular references and cells D4 through G4 now look like this:

Diluted Value	[Cl-]	[I-]	Vm
0.04110967	0.0411097	0.0262469	8.6511692

We are not quite finished. Near the **Iteration** command in the **Calculations** window was an instruction that said **Calc Now (Cmd + =)** on the Macintosh. This statement means that if you want the spreadsheet to execute more calculations ("calculate now"), press the **Command** key and the **equals** key at the same time. (On the PC the corresponding keyboard command is **F9**.) When you do this, the computer does another round of iteration to refine the numbers in cells D4 through G4. After pressing the keys about 10 times, the numbers in these cells stop changing and you have reached the final answer accurate to the number of decimal places displayed. The final values are:

Diluted Value	[Cl-]	[I-]	Vm
0.04110872	0.0411087	0.0262469	8.6514727

Exercises

A. Derive Equation 4.

B. Prepare a graph with Equation 4 for the titration of 50.00 mL of 0.050 00 M Br^- + 0.050 00 M Cl^- with 0.100 0 M Ag^+. Use your spreadsheet to find the fraction of each anion precipitated at the first equivalence point. (Answer: 99.723% of Br^- and 0.277% of Cl^- are precipitated.)

C. Derive an expression analogous to Equation 4 for titration of a mixture of three anions. Compute the shape of the titration curve for 50.00 mL of 0.050 00 M I^- + 0.050 00 M Br^- + 0.050 00 M Cl^- with 0.100 0 M Ag^+.

Solutions to Exercises

A. From Equation 2, mol MX (s) = $C_X^o\ V^o - [X^-](V_M + V^o)$

From Equation 3, mol MY (s) = $C_Y^o\ V^o - [Y^-](V_M + V^o)$

Substituting these into Equation 1 gives

$$C_M^o\ V_M =$$

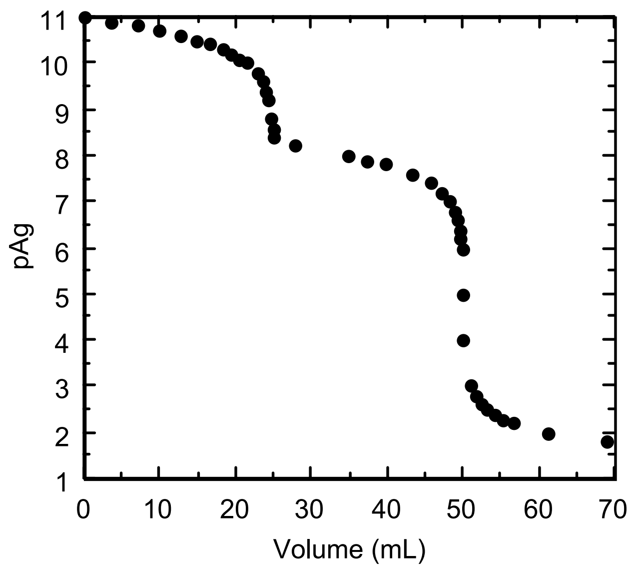
$$[M^+](V_M + V^o) + C_X^o\ V^o - [X^-](V_M + V^o) + C_Y^o\ V^o - [Y^-](V_M + V^o)$$

$$V_M(C_M^o - [M^+] + [X^-] + [Y^-]) = V^o([M^+] + C_X^o - [X^-] + C_Y^o - [Y^-])$$

which can be rearranged to give Equation 4.

B. Titration of 50.00 mL of 0.050 00 M Br^- + 0.050 00 M Cl^- with 0.100 0 M Ag^+

	A	B	C	D	E	F	G
1	Ksp(AgCl) =	pAg	[Ag+]	Cl-(Diluted)	[Cl-]	[Br-]	Vm
2	1.8E-10	11	1.00E-11	5.00E-02	5.00E-02	5.00E-02	0.000
3	Ksp(AgBr) =	10	1.00E-10	3.50E-02	3.50E-02	5.00E-03	21.429
4	5.E-13	9	1.00E-09	3.35E-02	3.35E-02	5.00E-04	24.627
5	Vo=	8	1.00E-08	2.95E-02	1.80E-02	5.00E-05	34.710
6	50	7	1.00E-07	2.55E-02	1.80E-03	5.00E-06	48.227
7	Co(Cl)=	5	1.00E-05	2.50E-02	1.80E-05	5.00E-08	49.992
8	0.05	4	1.00E-04	2.50E-02	1.80E-06	5.00E-09	50.098
9	Co(Br)=	3	1.00E-03	2.48E-02	1.80E-07	5.00E-10	51.010
10	0.05	2	1.00E-02	2.25E-02	1.80E-08	5.00E-11	61.111
11	Co(Ag)=						
12	0.1	Concentrations at first equivalence point:					
13		(Display more digits to answer question in problem)					
14		8.266402	5.41E-09	3.333E-02	3.324E-02	9.234E-05	25.000
15							
16	C2 = 10^-B2						
17	D2 = $A$8*($A$6/($A$6+G2))						
18	E2 = If((D2<($A$2/C2)),D2,$A$2/C2)						
19	F2 = $A$4/C2						
20	G2 = $A$6*($A$8+$A$10+C2-E2-F2)/($A$12-C2+E2+F2)						

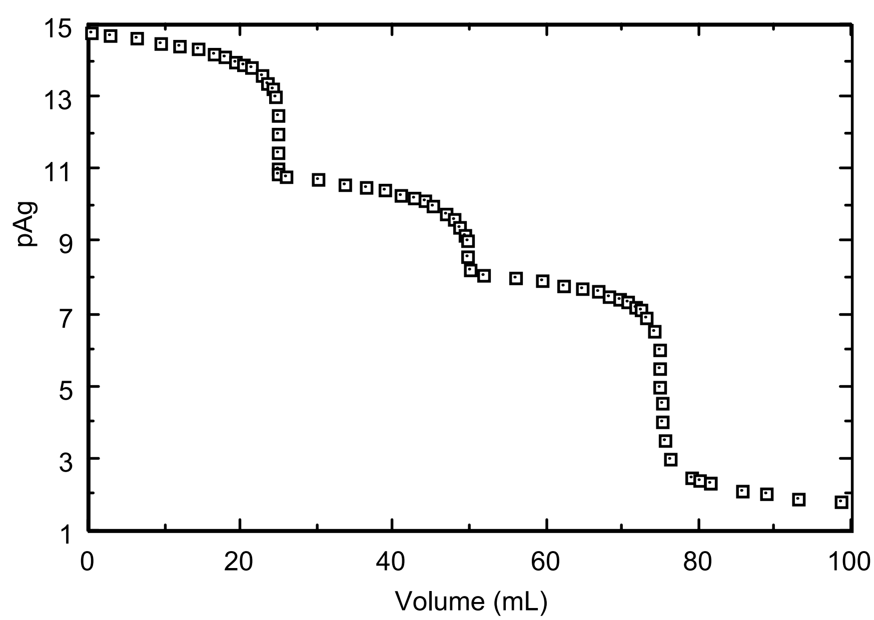

pAg
Volume (mL)
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70

C. For anions X^-, Y^- and Z^-, the titration equation is

$$V_M = V^o \left(\frac{C^o_X + C^o_Y + C^o_Z + [M^+] - [X^-] - [Y^-] - [Z^-]}{C^o_M - [M^+] + [X^-] + [Y^-] + [Z^-]} \right)$$

Spreadsheet for titration of anions X^-, Y^- and Z^- by Ag^+

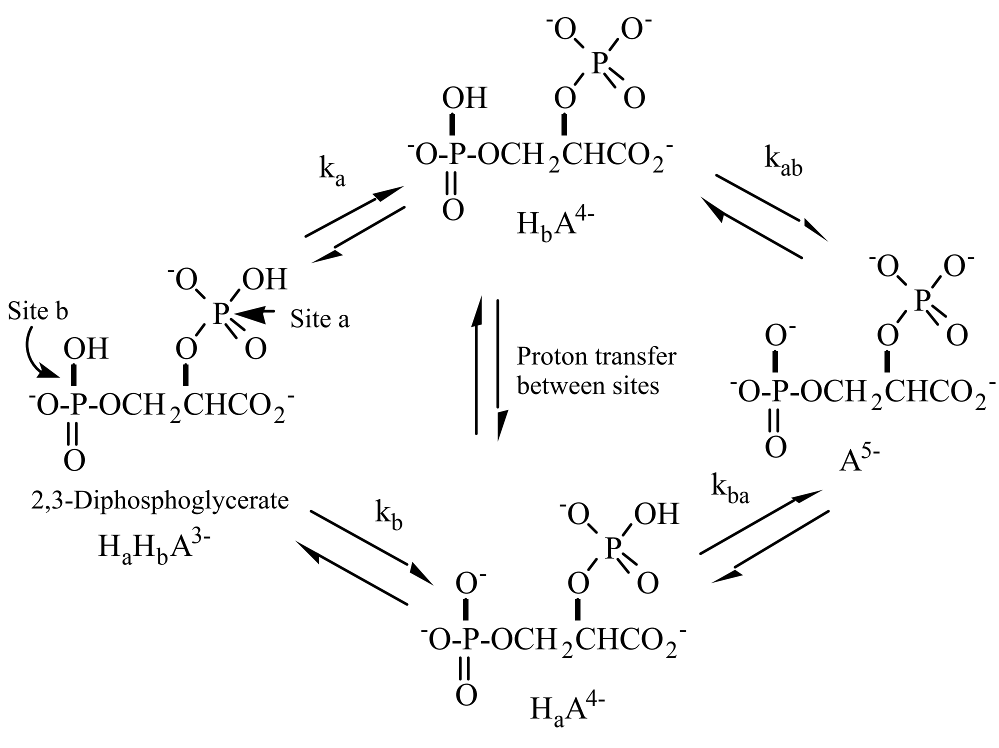
	A	B	C	D	E	F	G	H	I
1	Ksp(AgCl)	pAg	[Ag+]	[Cl-]	[Cl-]	[Br-]	[Br-]	[I-]	Vm
2	1.8E-10			(Diluted)		(Diluted)			
3	Ksp(AgBr)	14.77	1.7E-15	5.0E-02	5.0E-02	5.0E-02	5.0E-02	4.9E-02	0.38
4	5.E-13	14	1.0E-14	3.6E-02	3.6E-02	3.6E-02	3.6E-02	8.3E-03	19.25
5	Ksp(AgI)	13	1.0E-13	3.4E-02	3.4E-02	3.4E-02	3.4E-02	8.3E-04	24.38
6	8.3E-17	12	1.0E-12	3.3E-02	3.3E-02	3.3E-02	3.3E-02	8.3E-05	24.94
7	Vo =	11	1.0E-11	3.3E-02	3.3E-02	3.3E-02	3.3E-02	8.3E-06	24.99
8	50	10	1.0E-10	2.6E-02	2.6E-02	2.6E-02	5.0E-03	8.3E-07	45.24
9	Co(Cl) =	9	1.0E-09	2.5E-02	2.5E-02	2.5E-02	5.0E-04	8.3E-08	49.50
10	0.05	8	1.0E-08	2.4E-02	1.8E-02	2.4E-02	5.0E-05	8.3E-09	55.89
11	Co(Br) =	7	1.0E-07	2.0E-02	1.8E-03	2.0E-02	5.0E-06	8.3E-10	72.78
12	0.05	6	1.0E-06	2.0E-02	1.8E-04	2.0E-02	5.0E-07	8.3E-11	74.78
13	Co(I) =	5	1.0E-05	2.0E-02	1.8E-05	2.0E-02	5.0E-08	8.3E-12	74.99
14	0.05	4	1.0E-04	2.0E-02	1.8E-06	2.0E-02	5.0E-09	8.3E-13	75.12
15	Co(Ag) =	3	1.0E-03	2.0E-02	1.8E-07	2.0E-02	5.0E-10	8.3E-14	76.26
16	0.1	2	1.0E-02	1.8E-02	1.8E-08	1.8E-02	5.0E-11	8.3E-15	88.89
17									
18	C3 = 10^-B3					F3 = $A$12*($A$8/($A$8+I3))			
19	D3 = $A$10*($A$8/($A$8+I3))					G3 = If((F3<($A$4/C3)),F3,$A$4/C3)			
20	E3 = If((D3<($A$2/C3)),D3,$A$2/C3)					H3 = $A$6/C3			
21	I3 = $A$8*($A$10+$A$12+$A$14+C3-E3-G3-H3)/($A$16-C3+E3+G3+H3)								



Microequilibrium Constants

When two or more sites in a molecule have similar acid dissociation constants, there is an equilibrium of protons among those sites. Consider the molecule 2,3-diphosphoglycerate, which regulates the ability of your hemoglobin to bind O_2 in red blood cells. 2,3-Diphosphoglycerate reduces the affinity of hemoglobin for O_2. One method by which humans adapt to high altitudes is to decrease the concentration of 2,3-diphosphoglycerate in the blood and thereby increase the affinity of hemoglobin for the scarce O_2 in the air.

The species designated $H_aH_bA^{3-}$ at the left below is a diprotic acid that can lose a proton from phosphate at site a or site b.



A **microequilibrium constant** describes the reaction of a chemically distinct site in a molecule. Each site has a unique constant associated with it.

Loss of H_a from $H_aH_bA^{3-}$: $$k_a = \frac{[H_bA^{4-}][H^+]}{[H_aH_bA^{3-}]} = 2.9 \times 10^{-7}$$

Loss of H_b from $H_aH_bA^{3-}$: $$k_b = \frac{[H_aA^{4-}][H^+]}{[H_aH_bA^{3-}]} = 1.5 \times 10^{-7}$$

Loss of H_b from H_bA^{4-}: $$k_{ab} = \frac{[A^{5-}][H^+]}{[H_bA^{4-}]} = 7.5 \times 10^{-8}$$

Loss of H_a from H_aA^{4-}: $$k_{ba} = \frac{[A^{5-}][H^+]}{[H_aA^{4-}]} = 1.5 \times 10^{-7}$$

By contrast, ordinary equilibrium constants describe the gain or loss of protons without regard to which sites in the molecule participate in the chemistry. The microequilibrium constants are related to the conventional equilibrium constants as follows:

$$K_1 = \frac{([H_aA^{4-}] + [H_bA^{4-}])\,[H^+]}{[H_aH_bA^{3-}]} = k_a + k_b \qquad (1)$$

$$K_2 = \frac{[A^{5-}][H^+]}{[H_aA^{4-}] + [H_bA^{4-}]} = \frac{k_{ab}\,k_{ba}}{k_{ab} + k_{ba}} \qquad (2)$$

Microequilibrium constants can be measured by *nuclear magnetic resonance spectroscopy*, in which the spectroscopic signals for molecules protonated at site a can be distinguished from those protonated at site b.† The results of one such experiment are displayed in Figure 1, in which $H_aH_bA^{3-}$ was titrated with OH^-. Protons from both sites are lost simultaneously, but because k_a is about twice as great at k_b, there is always a greater concentration of H_bA^{4-} than of H_aA^{4-} throughout the reaction.

† A student experiment using nuclear magnetic resonance to find microequilibrium constants for N,N-dimethyl-1,3-propanediamine [$(CH_3)_2NCH_2CH_2CH_2NH_2$] is described by O. F. Onasch, H. M. Schwartz, D. A. Aikens, and S. C. Bunce, *J. Chem. Ed.* **1991**, *68*, 791. Spectro-photometric methods for measuring microequilibrium constants are clearly described by J. C. D'Angelo and T. W. Collette, *Anal. Chem*. **1997**, *69*, 1642 and J. Hernàndez-Borrell and M. T. Montero, *J. Chem. Ed.* **1997**, *74*, 1311.

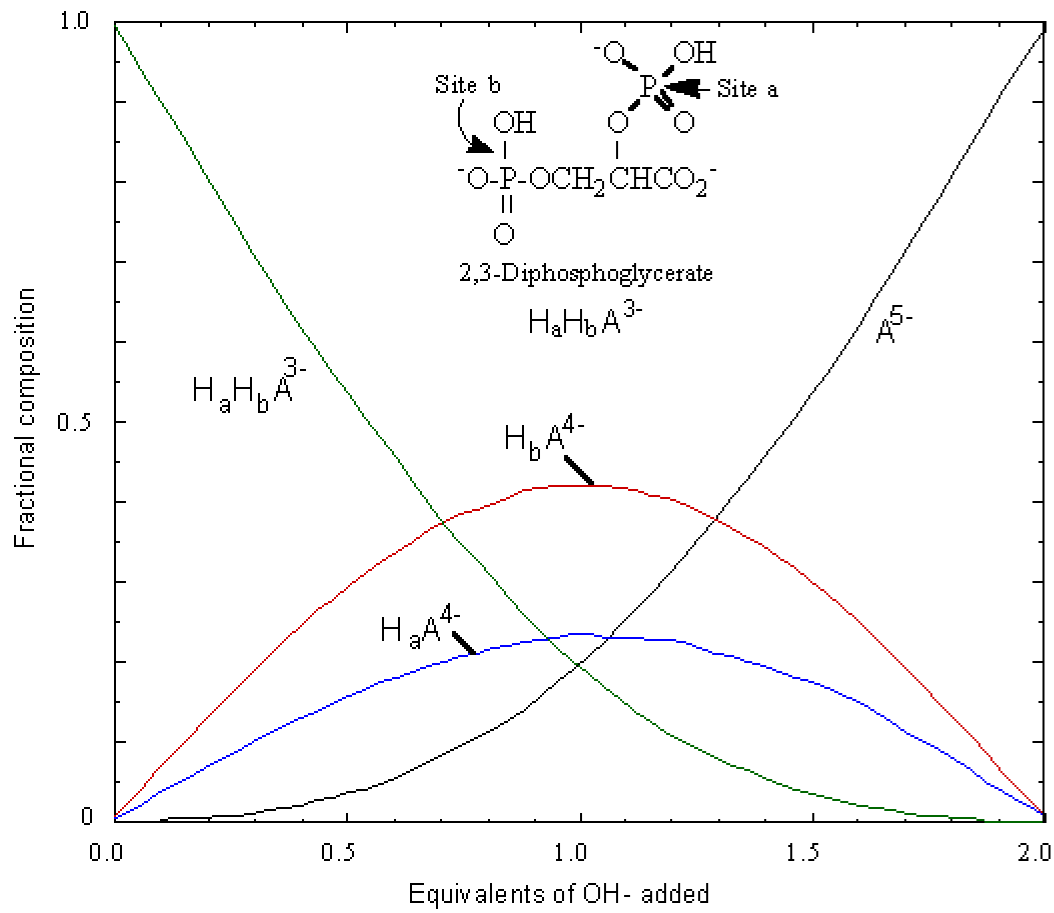


Figure 1. Fractional composition diagram for treatment of 2,3-diphosphoglycerate with base. Equilibrium among the species is described by microequilibrium constants. [From California State Science Fair project of Douglas Harris, 1992.]

Exercises

A. Derive Equations 1 and 2. Also, show that $k_a k_{ab} = k_b k_{ba}$. That is, there are only three independent microequilibrium constants. If you know three of them, you can calculate the fourth one.

B. Consider the diprotic acid H_2A, with two chemically distinguishable sites of protonation. We define the fraction of protonation at sites a and b as follows:

$$\text{Fraction of protonation at site a} = f_a = \frac{[H_2A] + [H_aA^-]}{[H_2A] + [H_aA^-] + [H_bA^-] + [A^{2-}]}$$

$$\text{Fraction of protonation at site a} = f_b = \frac{[H_2A] + [H_bA^-]}{[H_2A] + [H_aA^-] + [H_bA^-] + [A^{2-}]}$$

Show that

$$f_a = \frac{[H^+]^2 + k_b[H^+]}{[H^+]^2 + k_b[H^+] + k_a[H^+] + k_{ba}k_b}$$

$$f_b = \frac{[H^+]^2 + k_a[H^+]}{[H^+]^2 + k_b[H^+] + k_a[H^+] + k_{ba}k_b}$$

where k_a, k_b, k_{ab} and k_{ba} are microequilibrium constants. In the denominator of the f_b expression, we made use of the relation $k_a k_{ab} = k_b k_{ba}$ from the previous problem.

C. (a) Calculate K_1 and K_2 for 2,3-diphosphoglycerate.

(b) Using the expressions for f_a and f_b from the previous problem, calculate the fraction of protonation at each site at pH 7.00.

(c) Show that $[A^{2-}]/[H_2A] = k_{ba}k_b/[H^+]^2$ and find this quotient at pH 7.00. Based on this composition, estimate how many equivalents of OH^- in Figure 1 give pH 7.00.

Solutions to Exercises

A. $$k_a + k_b = \frac{[H_bA^{4-}][H^+]}{[H_aH_bA^{3-}]} + \frac{[H_aA^{4-}][H^+]}{[H_aH_bA^{3-}]} = \frac{([H_aA^{4-}] + [H_bA^{4-}])\,[H^+]}{[H_aH_bA^{3-}]} = K_1$$

$$\frac{k_{ab}k_{ba}}{k_{ab} + k_{ba}} = \frac{1}{\frac{1}{k_{ba}} + \frac{1}{k_{ab}}} = \frac{1}{\frac{[H_aA^{4-}]}{[A^{5-}][H^+]} + \frac{[H_bA^{4-}]}{[A^{5-}][H^+]}} = \frac{[A^{5-}][H^+]}{[H_aA^{4-}] + [H_bA^{4-}]} = K_2$$

$$k_a\,k_{ab} = \frac{\cancel{[H_bA^{4-}]}[H^+]}{[H_aH_bA^{3-}]}\,\frac{[A^{5-}][H^+]}{\cancel{[H_bA^{4-}]}} = \frac{\cancel{[H_aA^{4-}]}[H^+]}{[H_aH_bA^{3-}]}\,\frac{[A^{5-}][H^+]}{\cancel{[H_aA^{4-}]}} = k_b\,k_{ba}$$

B. $$f_a = \frac{[H_2A] + [H_aA^-]}{[H_2A] + [H_aA^-] + [H_bA^-] + [A^{2-}]}$$

$$\underset{\text{by } [H_2A]}{\overset{\text{divide everything}}{=}} \frac{1 + \frac{[H_aA^-]}{[H_2A]}}{1 + \frac{[H_aA^-]}{[H_2A]} + \frac{[H_bA^-]}{H_2A]} + \frac{[A^{2-}]}{[H_2A]}}$$

But $[H_aA^-]/[H_2A] = k_b/[H^+]$, $[H_bA^-]/[H_2A] = K_a/[H^+]$, and $[A^{2-}]/[H_2A] = k_bk_{ba}/[H^+]^2$. Substituting these expressions into the equation above gives

$$f_a = \frac{1 + \frac{k_b}{[H^+]}}{1 + \frac{k_b}{[H^+]} + \frac{k_a}{[H^+]} + \frac{k_bk_{ba}}{[H^+]^2}} \underset{\text{by } [H^+]^2}{\overset{\text{multiply everything}}{=}} \frac{[H^+] + k_b[H^+]}{[H^+]^2 + k_b[H^+] + k_a[H^+] + k_bk_{ba}}$$

The f_b expression is derived similarly.

C. (a) $K_1 = k_a + k_b = 4.4 \times 10^{-7}$; $K_2 = \frac{k_{ab}k_{ba}}{k_{ab} + k_{ba}} = 5.0 \times 10^{-8}$

(b) $$f_a = \frac{10^{-14} + 1.5 \times 10^{-14}}{10^{-14} + 1.5 \times 10^{-14} + 2.9 \times 10^{-14} + 2.25 \times 10^{-14}} = 0.33$$

$$f_b = \frac{10^{-14} + 2.9 \times 10^{-14}}{10^{-14} + 1.5 \times 10^{-14} + 2.9 \times 10^{-14} + 2.25 \times 10^{-14}} = 0.51$$

(c) $\frac{[A^{2-}]}{[H_2A]} = \frac{k_{ba}k_b}{[H^+]^2} = 2.25\cdot$ Measurements with a ruler on the graph show that $[A^{2-}]/[H_2A] \approx 2.25$ when equivalents of $OH^- \approx 1.15$.

Spreadsheets for Redox Titration Curves

This section derives equations for calculating titration curves with spreadsheets. Our goal is a single equation that describes an entire titration curve with no approximations, except neglect of activity coefficients.

Titration with an Oxidizing Agent

Consider an oxidizing titrant such as Ce^{4+} added to a reducing analyte such as Fe^{2+}. Let T be the titrant and A be the analyte, and let the oxidation states change by one electron:

$$\underset{\text{titrant}}{T} + \underset{\text{analyte}}{A} \rightarrow T^- + A^+ \qquad (1)$$

The reduction half-reactions for the two reagents are

$$T + e^- \rightleftharpoons T^- \qquad E = E^\circ_T - 0.059\,16 \log \frac{[T^-]}{[T]}$$

$$A^+ + e^- \rightleftharpoons A \qquad E = E^\circ_A - 0.059\,16 \log \frac{[A]}{[A^+]}$$

For a temperature other than 25°C, the factor 0.059 16 V is really (RT/F) ln 10, where R is the gas constant, T is temperature in kelvins, and F is the Faraday constant.

Now we rearrange the two Nernst equations to find more useful relationships between the concentrations of reactants and products:

$$E = E^\circ_T - 0.059\,16 \log \frac{[T^-]}{[T]} \Rightarrow \frac{[T^-]}{[T]} = \underbrace{10^{(E^\circ_T - E)/0.059\,16}}_{\text{This is } \tau} \Rightarrow [T^-] = \tau[T] \qquad (2)$$

$$E = E^\circ_A - 0.059\,16 \log \frac{[A]}{[A^+]} \Rightarrow \frac{[A]}{[A^+]} = \underbrace{10^{(E^\circ_A - E)/0.059\,16}}_{\text{This is } \alpha} \Rightarrow [A] = \alpha[A^+] \qquad (3)$$

where $\tau \equiv 10^{(E^\circ_T - E)/0.059\,16}$ and $\alpha \equiv 10^{(E^\circ_A - E)/0.059\,16}$. The letters tau and alpha were chosen as mnemonics for "titrant" and "analyte."

Next, we use Equations 2 and 3 and two mass balances to find expressions for the *products* of the titration reaction, $[T^-]$ and $[A^+]$.

mass balance for titrant:

$$[T] + [T^-] = T_{total}$$

$$\frac{1}{\tau}[T^-] + [T^-] = T_{total}$$

$$[T^-](\frac{1}{\tau} + 1) = T_{total} \quad \Rightarrow \quad [T^-] = \frac{\tau T_{total}}{1 + \tau}$$

mass balance for analyte:

$$[A] + [A^+] = A_{total} \quad \Rightarrow \quad [A^+] = \frac{A_{total}}{1 + \alpha}$$

Trying to contain our excitement, we carry on, for we have nearly derived a master equation for the titration. From the stoichiometry of Reaction 1, we know that $[T^-] = [A^+]$, *because they are created in a 1:1 mole ratio*. Equating $[T^-]$ and $[A^+]$, we find

$$[T^-] = [A^+]$$

$$\frac{\tau T_{total}}{1 + \tau} = \frac{A_{total}}{1 + \alpha} \qquad (4)$$

But the fraction of the way (ϕ) to the equivalence point is just the quotient T_{total}/A_{total}. That is, when the total concentration of T (= $[T] + [T^-]$) equals the total concentration of A (= $[A] + [A^+]$), we are at the equivalence point.

fraction of titration:

$$\phi = \frac{T_{total}}{A_{total}} \qquad \text{(= 1 at equivalence point)}$$

If the stoichiometry required, say, 2 mol of T for 3 mol of A, the fraction of titration would be $\phi = \frac{3T_{total}}{2A_{total}}$, because we demand that $\phi = 1$ at the equivalence point.

Rearranging Equation 4 to solve for the fraction of titration gives the master equation for the titration curve:

Titration with an oxidizing titrant:

$$\boxed{\phi = \frac{1 + \tau}{\tau(1 + \alpha)}} \qquad (5)$$

Equation 5 gives the fraction of titration as a function of the potential, E, which is buried in the numbers τ and α, defined in Equations 2 and 3. The titration curve is a graph of E versus ϕ. We will compute the curve in the reverse manner by inputting values of E and finding values of ϕ.

Let's amplify what ϕ means. If the equivalence point of a titration is 50 mL, then $\phi = 1$ at 50 mL. When 25 mL of titrant has been added, $\phi = 0.5$. When 55 mL of titrant has been added, $\phi = 1.1$. In the spreadsheet approach to redox titration curves, we input E and compute ϕ. If we know that the equivalence volume is V_e, then we compute the volume at any point in the titration from the relationship volume = ϕV_e.

EXAMPLE Spreadsheet Calculation of the Ce^{4+}/Fe^{2+} Titration Curve

Suppose that we titrate 100.0 mL of 0.050 0 M Fe^{2+} with 0.100 M Ce^{4+} using the cell in Figure 16-1 of the textbook. V_e = 50.0 mL, which means that $\phi = 1$ when $V_{Ce^{4+}}$ = 50.0 mL. Use Equation 5 to compute the voltages in Figure 16-2 of the textbook for titrant volumes of 50.0, 36.0, and 63.0 mL.

Solution The titration reaction is

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

and the half-reactions, written as reductions, are

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad \Rightarrow \tau = 10^{(E^\circ_T - E)/0.059\,16} = 10^{(1.70 - E)/0.059\,16}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad \Rightarrow \alpha = 10^{(E^\circ_A - E)/0.059\,16} = 10^{(0.767 - E)/0.059\,16}$$

In the spreadsheet in Figure 1, constants in column A are the standard reduction potentials, the quantity 0.059 16 V in the Nernst equation, and the equivalence volume, 50 mL. Values of E (versus S.H.E.) in column B are input to the spreadsheet. Columns C and D compute τ and α, and column E calculates ϕ with Equation 5. Column F converts E from the S.H.E. scale to the S.C.E. scale by subtracting 0.241 V. Column G multiplies ϕ by 50 mL to convert the fraction of titration into volume of titrant.

To find the voltage for a particular volume of titrant, we vary E in column B until the desired volume appears in column G. Rows 12–14 in the spreadsheet compute voltages for 50.0, 36.0, and 63.0 mL.

Because titration curves are steep near the equivalence point, *we recommend setting the precision of ϕ to 12 digits while varying E to search for the equivalence point potential*. Spreadsheets in this book were generated this way, and then the precision of ϕ was set back down to a reasonable number to display the results.

Equation 5 Applies to Many Oxidation Stoichiometries

Equation 5 applies to any titration in which T oxidizes A, providing neither reagent breaks into smaller fragments or associates into larger molecules. The stoichiometry of the reaction of T with A need not be 1:1, and there may be any number of electrons or other species (such as H^+ and H_2O) involved in the reaction. Thus, Equation 5 applies to the titration

$$\underset{\text{titrant}}{MnO_4^-} + \underset{\text{analyte}}{5Fe^{2+}} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

but not to the titration

$$\underset{\text{titrant}}{Cr_2O_7^{2-}} + \underset{\text{analyte}}{6Fe^{2+}} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

because $Cr_2O_7^{2-}$ breaks apart into two Cr^{3+} ions in the latter reaction. (The dichromate reaction is treated as a special case in Problem I below.

	A	B	C		E	F	G
1	E°(T) =	E (vs S.H.E.)	Tau	Alpha	Phi	E(vs S.C.E.)	Volume (mL)
2	1.7	0.600	3.92E+18	6.65E+02	0.00150	0.359	0.075
3	E°(A) =	0.700	8.00E+16	1.36E+01	0.06864	0.459	3.432
4	0.767	0.767	5.90E+15	1.00E+00	0.50000	0.526	25.000
5	Nernst =	0.800	1.63E+15	2.77E-01	0.78320	0.559	39.160
6	0.05916	1.000	6.80E+11	1.15E-04	0.99988	0.759	49.994
7	Ve =	1.200	2.83E+08	4.80E-08	1.00000	0.959	50.000
8	50	1.400	1.18E+05	2.00E-11	1.00001	1.159	50.000
9		1.600	4.90E+01	8.31E-15	1.02040	1.359	51.020
10		1.700	1.00E+00	1.70E-16	2.00000	1.459	100.000
11							
12		1.2335	7.68E+07	1.30E-08	1.00000	0.993	50.000
13		0.79127	2.29E+15	3.89E-01	0.72003	0.550	36.002
14		1.66539	3.85E+00	6.52E-16	1.26000	1.424	63.000
15							
16	C2 = 10^(($A$2-B2)/$A$6)			E2 = (1+C2)/(C2*(1+D2))			G2 = $A$8*E2
17	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.241			

Figure 1. Spreadsheet for titration of Fe^{2+} with Ce^{4+} based on Equation 5. Column B is the input and column E is the principal output. The fraction of titration in column E is converted to volume in column G, and potential (versus S.H.E.) in column B is converted to potential (versus. S.C.E.) in column F. A titration curve is a graph of column F versus column G.

When the Stoichiometry is Not 1:1

Suppose that Cu^+ is titrated with Tl^{3+} in 1 M $HClO_4$:

$$\underset{\text{titrant}}{Tl^{3+}} + \underset{\text{analyte}}{2Cu^+} \rightarrow Tl^+ + 2Cu^{2+}$$

The values of τ and α are computed from the half-reactions:

$$Tl^{3+} + 2e^- \rightleftharpoons Tl^+ \qquad E = 1.26 - \frac{0.059\,16}{2}\log\frac{[Tl^+]}{[Tl^{3+}]}$$

$$\Rightarrow\ \tau \equiv \frac{[Tl^+]}{[Tl^{3+}]} = 10^{2(1.26\ -\ E)/0.059\,16} \quad \text{(note } 2e^- \text{ in the exponent)} \tag{6}$$

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad E = 0.339 - 0.059\,16\log\frac{[Cu^+]}{[Cu^{2+}]}$$

$$\Rightarrow\ \alpha \equiv \frac{[Cu^+]}{[Cu^{2+}]} = 10^{(0.339\ -\ E)/0.059\,16} \tag{7}$$

Combining the mass balances with τ and α leads to the expressions

$$[Tl^+] = \frac{\tau Tl_{total}}{1+\tau} \qquad\qquad [Cu^{2+}] = \frac{Cu_{total}}{1+\alpha}$$

where $Tl_{total} = [Tl^{3+}] + [Tl^+]$ and $Cu_{total} = [Cu^{2+}] + [Cu^+]$.

Now we know that $[Cu^{2+}] = 2[Tl^+]$, because these products are created in a 2:1 mole ratio. Inserting the expressions above for $[Tl^+]$ and $[Cu^{2+}]$ into this equality gives

$$\frac{Cu_{total}}{1+\alpha} = \frac{2\tau Tl_{total}}{1+\tau} \tag{8}$$

Because the reaction requires one Tl^{3+} for two Cu^+ ions, the fraction of titration is

$$\phi + \frac{2Tl_{total}}{Cu_{total}} \overset{\text{from Eq. 8}}{=} \frac{(1+\tau)}{\tau\,(1+\alpha)}$$

The factor of 2 appears in the definition of ϕ because the fraction of titration is defined as unity at the equivalence point. The final result is identical to Equation 5, which was derived for 1:1 stoichiometry.

Adding H^+ and Other Reactants

Now consider the titration of Tl^+ by iodate in HCl solution:

$$\underset{\substack{\text{Iodate}\\\text{(titrant)}}}{IO_3^-} + \underset{\substack{\text{Thallous}\\\text{(analyte)}}}{2Tl^+} + 2Cl^- + 6H^+ \rightarrow ICl_2^- + \underset{\text{Thallic}}{2Tl^{3+}} + 3H_2O$$

Thallium is the analyte in this example. Its half-reaction is the same as in the preceding example, with a formal potential of 0.77 V in 1 M HCl.

$$Tl^{3+} + 2e^- \rightleftharpoons Tl^+ \qquad E = 0.77 - \frac{0.059\,16}{2}\log\frac{[Tl^+]}{[Tl^{3+}]}$$

$$\Rightarrow\ \alpha \equiv \frac{[Tl^+]}{[Tl^{3+}]} = 10^{2(0.77\ -\ E)/0.059\,16} \tag{9}$$

The iodate half reaction is more complicated:

$$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O \qquad E = 1.24 - \frac{0.059\,16}{4}\log\frac{[ICl_2^-]}{[IO_3^-][Cl^-]^2[H^+]^6}$$

We find τ by solving for the quotient $[ICl_2^-]/[IO_3^-]$, but now we must deal with extra terms involving $[Cl^-]$ and $[H^+]$:

$$\log\frac{[ICl_2^-]}{[IO_3^-][Cl^-]^2[H^+]^6} = \frac{4(1.24\text{-}E)}{0.059\,16}$$

$$\log\frac{[ICl_2^-]}{[IO_3^-]} - 2\log[Cl^-] - 6\log[H^+] = \frac{4(1.24\text{-}E)}{0.059\,16}$$

$$\log\frac{[ICl_2^-]}{[IO_3^-]} + 2\,pCl + 6\,pH = \frac{4(1.24\text{-}E)}{0.059\,16}$$

$$\underbrace{\log\frac{[ICl_2^-]}{[IO_3^-]}}_{} = \underbrace{\frac{4(1.24\text{-}E)}{0.059\,16} - 2\,pCl - 6\,pH}_{\tau}$$

$$\frac{[ICl_2^-]}{[IO_3^-]} = 10^{\{[4(1.24\text{-}E)/0.059\,16] - 2\,pCl - 6\,pH\}} \qquad (10)$$

To complete the derivation, we equate $[Tl^{3+}]$ to $2[IO_3^-]$ and define ϕ as $2I_{total}/Tl_{total}$ to find the same expression we found before, Equation 5. Note that $Tl_{total} = [Tl^{3+}] + [Tl^+]$ and $I_{total} = [IO_3^-] + [ICl_2^-]$.

EXAMPLE Spreadsheet Calculation of the IO_3^-/Tl^+ Titration Curve

Suppose that we titrate 100.0 mL of 0.010 0 M Tl^{2+} with 0.010 0 M IO_3^-, using Pt and saturated calomel electrodes. Assume that all solutions contain 1.00 M HCl, which means that pH = pCl = -log(1.00) = 0.00 in Equation 10. Because 1 mol of IO_3^- consumes 2 mol of Tl^+, the equivalence volume is 50.0 mL. Therefore $\phi = 1$ when $V_{IO_3^-} = 50.0$ mL. Use Equation 5 to compute the titration curve.

Solution The formulas for α and τ are given in Equations 9 and 10. The work is set out in Figure 2, in which we have added $[H^+]$ and $[Cl^-]$ as constants in column A.

	A	B	C		E	F	G
1	E°(T) =	E (vs S.H.E.)	Tau	Alpha	Phi	E(vs S.C.E.)	Volume (mL)
2	1.24	0.700	3.24E+36	2.33E+02	0.00428	0.459	0.214
3	E°(A) =	0.770	6.00E+31	1.00E+00	0.50000	0.529	25.000
4	0.77	0.800	5.62E+29	9.68E-02	0.91176	0.559	45.588
5	Nernst =	0.900	9.74E+22	4.03E-05	0.99996	0.659	49.998
6	0.05916	1.083	4.12E+10	2.62E-11	1.00000	0.842	50.000
7	Ve =	1.200	5.06E+02	2.91E-15	1.00197	0.959	50.099
8	50	1.24	1.00E+00	1.29E-16	2.00000	0.999	100.000
9	pCl =						
10	0		C2 = 10^(4*($A$2-B2)/$A$6-2*$A$10-6*$A$12)				
11	pH =		D2 = 10^(2*($A$4-B2)/$A$6)				
12	0		E2 = (1+C2)/(C2*(1+D2))				
13			F2 = B2-0.241				
14			G2 = $A$8*E2				

Figure 2. Spreadsheet for titration of Tl^{+} with iodate in Figure 16-3 of the textbook, based on Equation 5. Input in column B is varied to obtain output in column G at any desired volume. Note that the curve is not symmetric about the equivalence point because the stoichiometry of reactants is not 1:1.

Titration with a Reducing Agent

Following the same reasoning used above, we can show that if a reducing titrant is used, the general equation for the titration curve is

Titration with reducing titrant:

$$\boxed{\phi = \frac{\alpha\,(1+\tau)}{1+\alpha}} \tag{11}$$

where τ applies to the titrant and α applies to the analyte.

Titration of a Mixture

The titration of two species exhibits two breaks if the standard potentials of the redox couples are sufficiently different. Figure 3 shows the theoretical titration curve for an equimolar mixture of Tl^{+} and Sn^{2+} titrated with IO_3^- . The two *titration reactions* are

$$\text{first:} \quad IO_3^- + 2Sn^{2+} + 2Cl^- + 6H^+ \rightarrow ICl_2^- + 2Sn^{4+} + 3H_2O \tag{12}$$

$$\text{second:} \quad IO_3^- + 2Tl^{+} + 2Cl^- + 6H^+ \rightarrow ICl_2^- + 2Tl^{3+} + 3H_2O \tag{13}$$

and the relevant half-reactions are

$$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O \qquad E^\circ = 1.24\text{ V}$$

$$\Rightarrow \tau \equiv \frac{[ICl_2^-]}{[IO_3^-]} = 10^{\{[4(1.24-E)/0.059\,16] - 2\,pCl - 6\,pH\}}$$

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+} \qquad E^\circ = 0.139\text{ V}$$

$$\Rightarrow \alpha_1 \equiv \frac{[Sn^{2+}]}{[Sn^{4+}]} = 10^{2(0.139 - E)/0.059\,16}$$

$$Tl^{3+} + 2e^- \rightleftharpoons Tl^{+} \qquad E^\circ = 0.77\text{ V}$$

$$\Rightarrow \alpha_2 \equiv \frac{[Tl^{+}]}{[Tl^{3+}]} = 10^{2(0.77 - E)/0.059\,16}$$

Because the $Sn^{4+}|Sn^{2+}$ couple has a lower reduction potential than the $Tl^{3+}|Tl^{+}$ couple, Sn^{2+} will be oxidized before Tl^{+}. That is, the equilibrium constant for Reaction 12 is larger than for Reaction 13. This is another way of saying that Sn^{2+} is a stronger reducing agent than Tl^{+}.

To derive an equation for the titration of a mixture, the mass balance equates $[ICl_2^-]$ to the sum $\frac{1}{2}[Sn^{4+}] + \frac{1}{2}[Tl^{3+}]$, because 1 mol of ICl_2^- is generated for every 2 mol of Sn^{4+} and 1 mol of ICl_2^- is generated for every 2 mol of Tl^{3+}:

$$[ICl_2^-] = \frac{1}{2}[Sn^{4+}] + \frac{1}{2}[Tl^{3+}] \quad (14)$$

$$\frac{\tau I_{total}}{1+\tau} = \frac{1}{2}\left(\frac{Sn_{total}}{1+\alpha_1}\right) + \frac{1}{2}\left(\frac{Tl_{total}}{1+\alpha_2}\right)$$

Titration of a mixture:

$$\phi \equiv 2\left(\frac{I_{total}}{Sn_{total}}\right) = \frac{1+\tau}{\tau}\left(\frac{1}{1+\alpha_1} + \frac{Tl_{total}/Sn_{total}}{1+\alpha_2}\right) \quad (15)$$

↑ Factor of 2 appears because 1 mol of IO_3^- reacts with 2 mol of Sn^{2+} and ϕ must be unity at the equivalence point

Equation 15 describes the titration curve in Figure 3. The factors of $\frac{1}{2}$ in Equation 14 arise from the stoichiometry of reaction of titrant with each analyte. In general, these two fractions will not be $\frac{1}{2}$ and will be different from each other. The factor Tl_{total}/Sn_{total} gives the ratio of moles of analytes in the original solution.

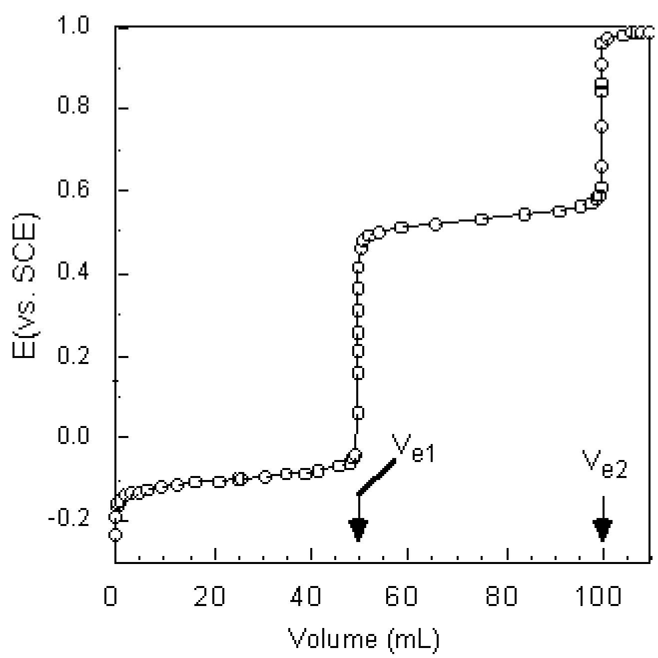


Figure 3
Theoretical curve for 100.0 mL containing 0.010 0 M Tl^+ plus 0.010 0 M Sn^{2+} titrated with 0.010 0 M IO_3^-, calculated with Equation 15. All solutions contain 1.00 M HCl.

Exercises

A. Use a spreadsheet to prepare a titration curve (potential referenced to saturated calomel electrode versus volume of titrant) for each case below. Compute the potential at $0.01V_e$, $0.5V_e$, $0.99V_e$, $0.999V_e$, V_e, $1.01V_e$, $1.1V_e$ and $2V_e$.

(a) Titration of 25.00 mL of 0.020 0 M Cr^{2+} with 0.010 00 M Fe^{3+} in 1 M $HClO_4$.

(b) Titration of 50.0 mL of 0.050 0 M Fe^{2+} (E° = 0.68 V) with 0.050 0 M MnO_4^- at pH 1.00 in H_2SO_4.

(c) Titration of 50 mL of 0.020 8 M Fe^{3+} with 0.017 3 M ascorbic acid at pH 1.00 in HCl.

(d) Titration of 50.0 mL of 0.050 M UO_2^{2+} in 1 M HCl with 0.100 M Sn^{2+} to give U^{4+} and Sn^{4+}.

B. Use a spreadsheet to prepare a titration curve (potential referenced to saturated Ag | AgCl electrode vs. volume of titrant) for each case below. In addition, compute the potential at the following specific points: 0.01 V_e, 0.5 V_e, 0.99 V_e, 0.999 V_e, V_e, 1.01 V_e, 1.1 V_e and 2 V_e.

(a) Titration of 25.00 mL of 0.020 0 M Fe^{3+} with 0.010 00 M Cr^{2+} in 1.00 M $HClO_4$.

(b) Titration of 10.0 mL of 0.050 0 M MnO_4^- with 0.050 0 M Fe^{2+} at pH -0.30 in H_2SO_4.

(c) Titration of 50 mL of 0.020 8 M Fe^{3+} with 0.017 3 M ascorbic acid at pH 0.00 in HCl.

(d) Titration of 50.0 mL of 0.050 M Sn^{2+} in 1 M HCl with 0.100 M UO_2^{2+} to give Sn^{4+} and U^{4+}.

C. Set up a spreadsheet to compute the curve for the titration of 100.0 mL of 0.010 0 M Tl^+ with 0.010 0 M IO_3^-. Investigate what happens if the constant concentration of HCl in both solutions is (a) 0.5, (b) 1.0, and (c) 2.0 M. Assume that the formal potential of the Tl^{3+} | Tl^+ couple remains at 0.77 V (which is a poor approximation).

D. Chromous ion (Cr^{2+}) was titrated with chlorate, ClO_3^-, at pH = -0.30 to give Cr^{3+} and Cl^-. The potential was measured with Pt and saturated Ag | AgCl electrodes.

(a) Write a balanced half-reaction for $ClO_3^- \rightarrow Cl^-$.

(b) Using just the information below, find E° for the ClO_3^- half-reaction.

$$ClO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 3H_2O \qquad E^\circ = 1.458\text{ V}$$

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^- \qquad E^\circ = 1.360\text{ V}$$

(c) Compute and graph the titration curve for titrant volume = 0 to volume = $2V_e$.

E. (a) A 100.0-mL solution containing 0.010 0 M Tl^+ plus 0.010 0 M Sn^{2+} in 1.00 M HCl was titrated with 0.010 0 M IO_3^- containing 1.00 M HCl. Prepare a spreadsheet to find the potential when 20.0, 25.0, 50.0, 60.0, 75.0, 100.0, and 110.0 mL of titrant has been added.

(b) Prepare a spreadsheet for the titration in (a) if the concentrations are changed to 5.00 mM Tl^+ and 15.0 mM Sn^{2+}. Find the potential at the following volumes: 20.0, 37.5, 74.0, 75.0, 76.0, 87.5, 100.0 and 110.0 mL.

F. A 25.0-mL solution containing a mixture of U^{4+} and Fe^{2+} in 1 M $HClO_4$ was titrated with 0.009 87 M $KMnO_4$ in 1 M $HClO_4$.

(a) Write balanced equations for the two titration reactions in the order in which they occur.

(b) Potentiometric end points were observed at 12.73 and 31.21 mL. Calculate the molarities of U^{4+} and Fe^{2+} in the unknown.

(c) Defining the fraction of titration, ϕ, such that $\phi = 1$ at the first equivalence point, show that

$$\phi = \frac{5}{2}\frac{Mn_{total}}{U_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{1}{1+\alpha_1} + \frac{1}{2}\frac{Fe_{total}/U_{total}}{1+\alpha_2}\right)$$

where α_1 refers to U^{4+} and α_2 refers to Fe^{2+}.

(d) Calculate the potential (versus S.H.E.) at $\frac{1}{2}V_{e1}$, V_{e1}, $V_{e1} + \frac{1}{2}V_{e2}$ (= 21.97 mL), and V_{e2} (= 31.21 mL), where V_{e1} and V_{e2} are the two equivalence volumes.

(e) Graph the titration curve up to 50 mL.

G. Consider the titration of analytes A and B by 1.00 M oxidizing titrant T:

$$T(aq) + 3e^- \rightleftharpoons T^{3-}(aq) \qquad E_T^\circ = 0.93\text{ V}$$

$$\Rightarrow \tau = \frac{[T^{3-}]}{[T]} = 10^{3(0.93 - E)/0.059\,16}$$

$$A^{2+}(aq) + 2e^- \rightleftharpoons A(aq) \qquad E_A^\circ = -0.13\text{ V}$$

$$\Rightarrow \alpha = \frac{[A]}{[A^{2+}]} = 10^{2(-0.13 - E)/0.059\,16}$$

$$B^+(aq) + e^- \rightleftharpoons B(aq) \qquad E_B^\circ = 0.46\text{ V}$$

$$\Rightarrow \beta = \frac{[B]}{[B^+]} = 10^{(0.46 - E)/0.059\,16}$$

The initial volume of 100.0 mL contains 0.300 M A and 0.060 0 M B.

(a) Write the two titration reactions in the order in which they occur. Calculate the equilibrium constant for each one.

(b) Find the two equivalence volumes, designated V_{e1} and V_{e2}.

(c) Defining the fraction of titration (ϕ) to be unity at the first equivalence point, show that

$$\phi = \frac{3}{2}\frac{T_{total}}{A_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{1}{1+\alpha} + \frac{1}{2}\frac{B_{total}/A_{total}}{1+\beta}\right)$$

(d) Use a spreadsheet to prepare a graph of the titration curve (E versus S.H.E.).

(e) What are the potentials at the two equivalence points? Use 12 decimal places for V_e to obtain 3 digits for the equivalence point potential.

H. Suppose that 100.0 mL of solution containing 0.100 M Fe^{2+} and 5.00×10^{-5} M tris (1,10-phenanthroline)Fe(II) (ferroin) is titrated with 0.050 0 M Ce^{4+} in 1 M $HClO_4$. Calculate the potential (versus S.H.E.) at the following volumes of Ce^{4+} and prepare a graph of the titration curve: 1.0, 10.0, 100.0, 190.0, 199.0, 200.0, 200.05, 200.10, 200.15, 200.2, 201.0, and 210.0 mL. Is ferroin a suitable indicator for the titration?

I. *Derivation of Spreadsheet Equation for Dichromate Titrations.* Consider the titration of 120.0 mL of 0.010 0 M Fe^{2+} by 0.020 0 M dichromate at pH = 1.00:

$$\underset{\text{Titrant}}{Cr_2O_7^{2-}} + \underset{\text{Analyte}}{6Fe^{2+}} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The half-reaction for analyte is $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\qquad E^\circ = 0.771$ V

$$\Rightarrow \alpha = \frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{(0.771 - E)/0.059\,16}$$

$$[Fe^{3+}] = Fe_{total}/(1+\alpha).$$

The half-reaction for titrant is more complicated:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\circ = 1.36 \text{ V}$$

$$E = E^\circ - \frac{0.059\,16}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$\Rightarrow \tau \equiv \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]} = 10^{\{6(1.36 - E)/0.059\,16 - 14pH\}}$$

$$\Rightarrow [Cr_2O_7^{2-}] = \frac{1}{\tau}[Cr^{3+}]^2$$

The mass balance for chromium is

$$Cr_{total} = [Cr^{3+}] + 2[Cr_2O_7^{2-}] = [Cr^{3+}] + \frac{2}{\tau}[Cr^{3+}]^2 \qquad (A)$$

$$\Rightarrow Cr_{total} = [Cr^{3+}]\left(\frac{\tau + 2[Cr^{3+}]}{\tau}\right)$$

$$\Rightarrow [Cr^{3+}] = Cr_{total}\left(\frac{\tau}{\tau + 2[Cr^{3+}]}\right) \qquad (B)$$

Quadratic equation A can be solved for $[Cr^{3+}]$ and we find the positive root to be

$$[Cr^{3+}] = \frac{-\frac{\tau}{2} + \sqrt{\frac{\tau^2}{4} + 2\tau Cr_{total}}}{2} \qquad (C)$$

Since Fe^{3+} and Cr^{3+} are created in 6:2 proportions, we can say that

$$3[Cr^{3+}] = [Fe^{3+}]$$

Substituting $[Cr^{3+}]$ from Equation B and $[Fe^{3+}] = Fe_{total}/(1+\alpha)$ gives

$$3\,Cr_{total}\left(\frac{\tau}{\tau + 2[Cr^{3+}]}\right) = \frac{Fe_{total}}{(1+\alpha)}$$

The fraction of titration for the reaction is $\phi = 3Cr_{total}/Fe_{total}$. The factor of 3 guarantees that $\phi = 1$ at the equivalence point. Rearranging the equation above gives

$$\phi = \frac{3\,Cr_{total}}{Fe_{total}} = \frac{\tau + 2[Cr^{3+}]}{\tau(1+\alpha)}$$

Replacing $[Cr^{3+}]$ by its value from Equation C gives what we seek:

$$\phi = \frac{3\,Cr_{total}}{Fe_{total}} = \frac{\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2Cr_{total}}{\tau}}}{1+\alpha} \qquad (D)$$

But the value of ϕ depends on the total concentration of chromium at each point. We can express the total concentration of chromium in terms of ϕ as follows:

$$Cr_{total} = \frac{\text{mmol of Cr}}{\text{mL of solution}} = \frac{V_{Cr}\,C_{Cr}}{V_{Cr} + V_{Fe}^{\circ}} = \frac{\phi\,V_e\,C_{Cr}}{\phi\,V_e + V_{Fe}^{\circ}} \qquad (E)$$

where C_{Cr} is the concentration of chromium ($= 2[Cr_2O_7^{2-}]$) in titrant and V_{Fe}° is the initial concentration of Fe^{2+} analyte. Substituting Cr_{total} from Equation E into Equation D gives the master equation for the titration curve of Fe^{2+} titrated with $Cr_2O_7^{2-}$:

$$\boxed{\phi = \frac{3\,Cr_{total}}{Fe_{total}} = \frac{\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2\,\phi\,V_e\,C_{Cr}}{\tau\,\phi\,V_e + \tau\,V_{Fe}^{\circ}}}}{1+\alpha}} \qquad (F)$$

To implement Equation F on a spreadsheet, the constants C_{Cr} and V_{Fe}° are added to column A. A value of potential (vs S.H.E.) is inserted in column B and values of τ and α are computed in columns C and D. Equation F is used to compute ϕ in column E. In this formula, ϕ is defined in terms of itself. We call this a *circular definition*. The spreadsheet uses successive approximations to find a solution. The end of the section "Spreadsheet for Precipitation Titration of a Mixture" in this supplement explains how to handle a circular definition in a spreadsheet.

Consider the titration of 120.0 mL of 0.0100 M Fe^{2+} (buffered to pH 1.00) with 0.020 M $Cr_2O_7^{2-}$ monitored by Pt and saturated Ag | AgCl electrodes. Use a spreadsheet to prepare a graph of the titration curve. Report the potential at the following volumes of $Cr_2O_7^{2-}$: 0.100, 2.00, 4.00, 6.00, 8.00, 9.00, 9.90, 10.00, 10.10, 11.00, 12.00 mL.

Solutions to Exercises

A. (a) Titration reaction: $Cr^{2+} + Fe^{3+} \rightarrow Fe^{2+} + Cr^{3+}$

Titrant: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\circ = 0.767$ V

Analyte: $Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\circ = -0.42$ V

$\tau = 10^{(0.767 - E)/0.059\,16}$ $\alpha = 10^{(-0.42 - E)/0.059\,16}$

$$\phi = \frac{(1+\tau)}{\tau\,(1+\alpha)}$$ $V_e = 50.0$ mL

Spreadsheet for titration of Cr^{2+} with Fe^{3+}

	A	B	C	D	E	F	G
1	E°(T) =	E (vs S.H.E.)	Tau	Alpha	Phi	E (vs S.C.E.)	Volume (mL)
2	0.767	-0.538	1.15E+22	9.88E+01	0.01002	-0.779	0.501
3	E°(A) =	-0.420	1.16E+20	1.00E+00	0.50000	-0.661	25.000
4	-0.42	-0.302	1.17E+18	1.01E-02	0.98998	-0.543	49.499
5	Nernst =	-0.242	1.14E+17	9.80E-04	0.99902	-0.483	49.951
6	0.05916	0.174	1.06E+10	9.11E-11	1.00000	-0.067	50.000
7	Ve =	0.649	9.88E+01	8.52E-19	1.01013	0.408	50.506
8	50	0.708	9.94E+00	8.57E-20	1.10062	0.467	55.031
9		0.767	1.00E+00	8.63E-21	2.00000	0.526	100.000
10							
11	C2 = 10^(($A$2-B2)/$A$6)			E2 = (1+C2)/(C2*(1+D2))			
12	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.241		G2 = $A$8*E2	

(b) Titration reaction: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Titrant: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^\circ = 1.507$ V

Analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\circ = 0.68$ V

$\tau = 10^{\{[5(1.507 - E)/0.059\,16] - 8\,pH\}}$ $\alpha = 10^{(0.68 - E)/0.059\,16}$

$$\phi = \frac{(1+\tau)}{\tau\,(1+\alpha)}$$ $V_e = 10.0$ mL

Spreadsheet for titration of Fe^{2+} with permanganate

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E (vs S.C.E.)	Volume (mL)
2	1.507	0.562	7.38E+71	9.88E+01	0.01002	0.321	0.100
3	E°(A) =	0.680	7.86E+61	1.00E+00	0.50000	0.439	5.000
4	0.68	0.798	8.36E+51	1.01E-02	0.98998	0.557	9.900
5	Nernst =	0.858	7.10E+46	9.80E-04	0.99902	0.617	9.990
6	0.05916	1.290	2.19E+10	4.89E-11	1.00000	1.049	10.000
7	Ve =	1.389	9.40E+01	1.04E-12	1.01064	1.148	10.106
8	10	1.400	1.10E+01	6.75E-13	1.09052	1.159	10.905
9	pH =	1.412	1.07E+00	4.23E-13	1.93525	1.171	19.352
10	1						
11	C2 = 10^(5*($A$2-B2)/$A$6-8*$A$10)				E2 = (1+C2)/(C2*(1+D2))		
12	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.241		G2 = $A$8*E2	

(c) Titration reaction: ascorbic acid + $2Fe^{3+}$ + H_2O $\rightarrow$ dehydro. + $2Fe^{2+}$ + $2H^+$

Titrant: dehydro. + $2H^+$ + $2e^-$ $\rightarrow$ ascorbic acid + H_2O $\quad E^\circ = 0.390$ V

Analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\circ = 0.732$ V

$\tau = 10^{\{[2(0.390 - E)/0.059\ 16] - 2\ pH\}}$ $\quad \alpha = 10^{(0.732 - E)/0.059\ 16}$

$$\phi = \frac{\alpha(1+\tau)}{(1+\alpha)} \qquad V_e = 30.0_6 \text{ mL}$$

Spreadsheet for titration of Fe^{3+} with ascorbic acid

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E (vs S.C.E.)	Volume (mL)
2	0.39	0.850	2.81E-18	1.01E-02	0.01002	0.609	0.301
3	E°(A) =	0.732	2.74E-14	1.00E+00	0.50000	0.491	15.030
4	0.732	0.614	2.67E-10	9.88E+01	0.98998	0.373	29.759
5	Nernst =	0.555	2.64E-08	9.81E+02	0.99898	0.314	30.029
6	0.05916	0.464	3.15E-05	3.39E+04	1.00000	0.223	30.060
7	Ve =	0.390	1.00E-02	6.04E+05	1.01000	0.149	30.361
8	30.06	0.360	1.03E-01	1.94E+06	1.10332	0.119	33.166
9	pH =	0.331	9.88E-01	6.00E+06	1.98762	0.090	59.748
10	1						
11	C2 = 10^(2*($A$2-B2)/$A$6-2*$A$10)				E2 = D2*(1+C2)/(1+D2)		
12	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.241		G2 = $A$8*E2	

(d) Titration reaction: UO_2^{2+} + Sn^{2+} + $4H^+$ $\rightarrow$ U^{4+} + Sn^{4+} + $2H_2O$

Titrant: $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $\quad E^\circ = 0.139$ V

Analyte: $UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$ $\quad E^\circ = 0.273$ V

$\tau = 10^{[2(0.139 - E)/0.059\ 16]}$ $\quad \alpha = 10^{\{2(0.273 - E)/0.059\ 16 - 4\ pH\}}$

$$\phi = \frac{\alpha(1+\tau)}{(1+\alpha)} \qquad V_e = 25.0 \text{ mL}$$

Spreadsheet for titration of UO_2^{2+} with Sn^{2+}

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E (vs S.C.E.)	Volume (mL)
2	0.139	0.332	2.99E-07	1.01E-02	0.01002	0.091	0.251
3	E°(A) =	0.301	3.34E-06	1.13E-01	0.10160	0.060	2.540
4	0.273	0.216	2.49E-03	8.45E+01	0.99077	-0.025	24.769
5	Nernst =	0.207	5.03E-03	1.70E+02	0.99916	-0.034	24.979
6	0.05916	0.206	5.43E-03	1.84E+02	1.00000	-0.035	25.000
7	Ve =	0.195	1.28E-02	4.33E+02	1.01046	-0.046	25.261
8	25	0.169	9.68E-02	3.28E+03	1.09645	-0.072	27.411
9	pH =	0.139	1.00E+00	3.39E+04	1.99994	-0.102	49.999
10	0						
11	C2 = 10^(2*($A$2-B2)/$A$6-4*$A$10)				E2 = D2*(1+C2)/(1+D2)		
12	D2 = 10^(2*($A$4-B2)/$A$6)			F2 = B2-0.241		G2 = $A$8*E2	

B. (a) Titration reaction: $Cr^{2+} + Fe^{3+} \rightarrow Fe^{2+} + Cr^{3+}$

Titrant: $Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\circ = -0.42$ V

Analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\circ = 0.767$ V

$\tau = 10^{(-0.42 - E)/0.059\,16}$ $\alpha = 10^{(0.767 - E)/0.059\,16}$

$$\phi = \frac{\alpha\,(1 + \tau)}{(1 + \alpha)}$$ $V_e = 50.0$ mL

Spreadsheet for titration of Fe^{3+} with Cr^{2+}

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E(vs Ag|AgCl)	Volume (mL)
2	-0.42	0.885	8.73E-23	1.01E-02	0.01002	0.688	0.501
3	E°(A) =	0.767	8.63E-21	1.00E+00	0.50000	0.570	25.000
4	0.767	0.649	8.52E-19	9.88E+01	0.98998	0.452	49.499
5	Nernst =	0.590	8.47E-18	9.81E+02	0.99898	0.393	49.949
6	0.05916	0.174	9.11E-11	1.06E+10	1.00000	-0.023	50.000
7	Ve =	-0.302	1.01E-02	1.17E+18	1.01013	-0.499	50.506
8	50	-0.361	1.01E-01	1.17E+19	1.10062	-0.558	55.031
9		-0.420	1.00E+00	1.16E+20	2.00000	-0.617	100.000
10							
11	C2 = 10^(($A$2-B2)/$A$6)			E2 = D2*(1+C2)/(1+D2)			
12	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.197		G2 = $A$8*E2	

(b) Titration reaction: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Titrant: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\circ = 0.68$ V

Analyte: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^\circ = 1.507$ V

$\tau = 10^{(0.68 - E)/0.059\,16}$ $\alpha = 10^{\{[5(1.507 - E)/0.059\,16] - 8\,pH\}}$

$$\phi = \frac{\alpha\,(1 + \tau)}{(1 + \alpha)}$$ $V_e = 50.0$ mL

Spreadsheet for titration of permanganate with Fe^{2+}

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E(vs Ag|AgCl)	Volume (mL)
2	0.68	1.559	1.39E-15	1.01E-02	0.01002	1.362	0.501
3	E°(A) =	1.535	3.53E-15	1.08E+00	0.51930	1.338	25.965
4	1.507	1.512	8.64E-15	9.49E+01	0.98958	1.315	49.479
5	Nernst =	1.499	1.43E-14	1.19E+03	0.99916	1.302	49.958
6	0.05916	1.390	9.97E-13	1.94E+12	1.00000	1.193	50.000
7	Ve =	0.798	1.01E-02	2.10E+62	1.01013	0.601	50.506
8	50	0.739	1.01E-01	2.04E+67	1.10062	0.542	55.031
9	pH =	0.680	1.00E+00	1.97E+72	2.00000	0.483	100.000
10	-0.3						
11	C2 = 10^(($A$2-B2)/$A$6)			F2 = B2-0.197		G2 = $A$8*E2	
12	D2 = 10^(5*($A$4-B2)/$A$6-8*$A$10)				E2 = D2*(1+C2)/(1+D2)		

(c) Titration reaction: dehydro. + $2Fe^{2+}$ + $2H^+$ $\rightarrow$ ascorbic acid + $2Fe^{3+}$ + H_2O

Titrant: dehydro. + $2H^+$ + $2e^-$ $\rightarrow$ ascorbic acid + H_2O $\quad E^\circ = 0.390$ V

Analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\circ = 0.732$ V

$\tau = 10^{\{[2(0.390 - E)/0.059\,16] - 2\,pH\}}$ $\quad \alpha = 10^{(0.732 - E)/0.059\,16}$

$$\phi = \frac{\alpha(1+\tau)}{(1+\alpha)}$$

$V_e = 30.0_6$ mL

Spreadsheet for titration of Fe^{3+} with ascorbic acid

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E(vs Ag|AgCl)	Volume (mL)
2	0.39	0.850	2.81E-16	1.01E-02	0.01002	0.653	0.301
3	E°(A) =	0.732	2.74E-12	1.00E+00	0.50000	0.535	15.030
4	0.732	0.614	2.67E-08	9.88E+01	0.98998	0.417	29.759
5	Nernst =	0.554	2.86E-06	1.02E+03	0.99902	0.357	30.031
6	0.05916	0.504	1.40E-04	7.14E+03	1.00000	0.307	30.060
7	Ve =	0.449	1.01E-02	6.08E+04	1.01011	0.252	30.364
8	30.06	0.420	9.68E-02	1.88E+05	1.09678	0.223	32.969
9	pH =	0.390	1.00E+00	6.04E+05	2.00000	0.149	60.120
10	0						
11	C2 = 10^(2*($A$2-B2)/$A$6-2*$A$10)				E2 = D2*(1+C2)/(1+D2)		
12	D2 = 10^(($A$4-B2)/$A$6)			F2 = B2-0.197		G2 = $A$8*E2	

(d) Titration reaction: UO_2^{2+} + Sn^{2+} + $4H^+$ $\rightarrow$ U^{4+} + Sn^{4+} + $2H_2O$

Titrant: UO_2^{2+} + $4H^+$ + $2e^-$ $\rightarrow$ U^{4+} + $2H_2O$ $\quad E^\circ = 0.273$ V

Analyte: $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $\quad E^\circ = 0.139$ V

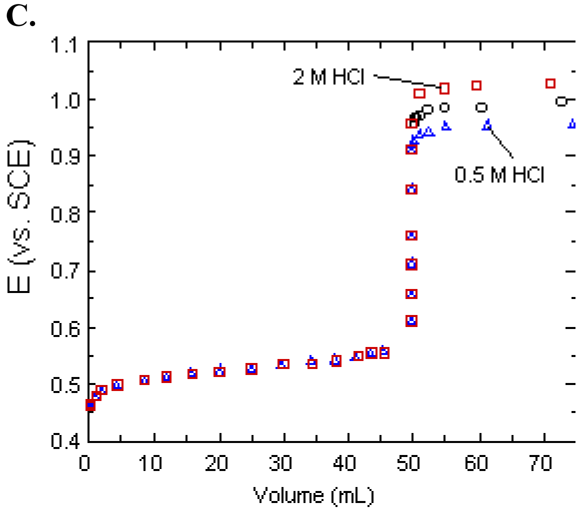
$\tau = 10^{\{2(0.273 - E)/0.059\,16 - 4\,pH\}}$ $\quad \alpha = 10^{[2(0.139 - E)/0.059\,16]}$

$$\phi = \frac{(1+\tau)}{\tau\,(1+\alpha)} \qquad\qquad V_e = 25.0 \text{ mL}$$

Spreadsheet for titration of Sn^{2+} with UO_2^{2+}

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E(vs Ag|AgCl)	Volume (mL)
2	0.273	0.080	3.35E+06	9.88E+01	0.01002	-0.117	0.251
3	E°(A) =	0.139	3.39E+04	1.00E+00	0.50001	-0.058	12.500
4	0.139	0.195	4.33E+02	1.28E-02	0.98965	-0.002	24.741
5	Nernst =	0.205	1.99E+02	5.87E-03	0.99916	0.008	24.979
6	0.05916	0.206	1.84E+02	5.43E-03	1.00000	0.009	25.000
7	Ve =	0.217	7.82E+01	2.31E-03	1.01046	0.020	25.261
8	25	0.243	1.03E+01	3.05E-04	1.09645	0.046	27.411
9	pH =	0.273	1.00E+00	2.95E-05	1.99994	0.076	49.999
10	0						
11	C2 = 10^(2*($A$2-B2)/$A$6-4*$A$10)				E2 = (1+C2)/(C2*(1+D2))		
12	D2 = 10^(2*($A$4-B2)/$A$6)			F2 = B2-0.197		G2 = $A$8*E2	

C.



D. (a) Balanced reaction: $ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O$

(b) $ClO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}\,Cl_2 + 3H_2O \qquad \Delta G_1^\circ = -5F(1.458)$

$\frac{1}{2}\,Cl_2 + e^- \rightarrow Cl^- \qquad \Delta G_2^\circ = -1F(1.360)$

$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \quad \Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ = -6FE_3^\circ$

$-6FE_3^\circ = -5F\,(1.458) - F\,(1.360) \Rightarrow E_3^\circ = 1.442$ V

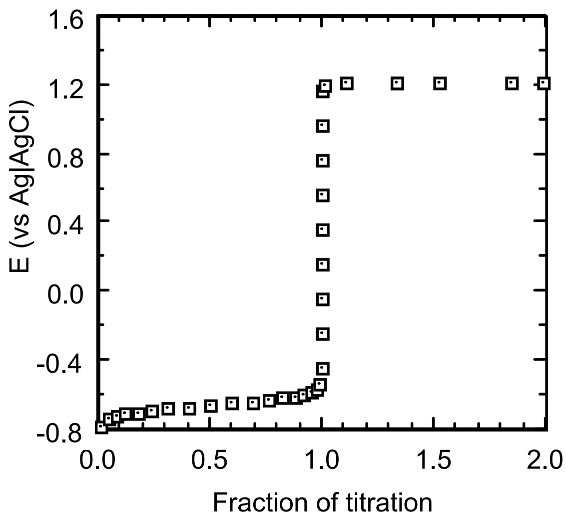
(c) Titration reaction: $ClO_3^- + 6H^+ + 6Cr^{2+} \rightleftharpoons Cl^- + 6Cr^{3+} + 3H_2O$

Titrant: $ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\circ = 1.442$ V

Analyte: $Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\circ = -0.42$ V

$\tau = 10^{\{[6(1.442 - E)/0.059\,16] - 6\text{ pH}\}}$ $\alpha = 10^{(-0.42 - E)/0.059\,16}$

$$\phi = \frac{(1+\tau)}{\tau\,(1+\alpha)}$$



E. (a) Spreadsheet for titration of $Tl^+ + Sn^{2+}$ with iodate

	A	B	C	D	E	F	G	H
1	E°(T) =	E(SHE)	Tau	Alpha1	Alpha2	Phi	E(SCE)	Volume
2	1.24	0.134	6.0E+74	1.5E+00	3.2E+21	0.4039	-0.107	20.195
3	E°(A1) =	0.139	2.8E+74	1.0E+00	2.1E+21	0.5000	-0.102	25.000
4	0.139	0.454	1.4E+53	2.2E-11	4.8E+10	1.0000	0.213	50.000
5	E°(A2) =	0.752	9.9E+32	1.9E-21	4.1E+00	1.1976	0.511	59.882
6	0.77	0.770	6.0E+31	4.7E-22	1.0E+00	1.5000	0.529	75.000
7	Nernst =	1.080	6.6E+10	1.5E-32	3.3E-11	2.0000	0.839	100.000
8	0.05916	1.225	1.0E+01	1.9E-37	4.1E-16	2.1936	0.984	109.678
9	Ve =							
10	50							
11	pCl =		C2 = 10^(4*($A$2-B2)/$A$8-2*$A$12-6*$A$14)					
12	0		D2 = 10^(2*($A$4-B2)/$A$8)					
13	pH =		E2 = 10^(2*($A$6-B2)/$A$8)					
14	0		F2 = ((1+C2)/C2)*((1/(1+D2))+(($A$16/$A$18)/(1+E2)))					
15	Tl(total)=		G2 = B2-0.241					
16	0.01		H2 = $A$10*F2					
17	Sn(total)=							
18	0.01							

(b) Titration of Tl^+ and Sn^{2+} with iodate

	A	B	C	D	E	F	G	H
1	E°(T) =	E(S.H.E.)	Tau	Alpha1	Alpha2	Phi	E(S.C.E.)	Volume
2	1.24	0.126	2.1E+75	2.8E+00	5.9E+21	0.27	-0.115	19.995
3	E°(A1) =	0.139	2.8E+74	1.0E+00	2.1E+21	0.50	-0.102	37.500
4	0.139	0.194	5.3E+70	1.4E-02	3.0E+19	0.99	-0.047	73.977
5	E°(A2) =	0.462	4.0E+52	1.2E-11	2.6E+10	1.00	0.221	75.000
6	0.77	0.729	3.6E+34	1.1E-20	2.4E+01	1.01	0.488	75.987
7	Nernst =	0.770	6.0E+31	4.7E-22	1.0E+00	1.17	0.529	87.500
8	0.05916	1.077	1.0E+11	1.9E-32	4.2E-11	1.33	0.836	100.000
9	Ve =	1.226	8.8E+00	1.8E-37	3.8E-16	1.48	0.985	111.309
10	75							
11	pCl =							
12	0		C2 = 10^(4*($A$2-B2)/$A$8-2*$A$12-6*$A$14)					
13	pH =		D2 = 10^(2*($A$4-B2)/$A$8)					
14	0		E2 = 10^(2*($A$6-B2)/$A$8)					
15	Tl(total)=		F2 = ((1+C2)/C2)*((1/(1+D2))+(($A$16/$A$18)/(1+E2)))					
16	0.005		G2 = B2-0.241					
17	Sn(total)=		H2 = $A$10*F2					
18	0.015							

F. Titrant: $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^\circ = 1.507\text{ V}$

$$\tau = 10^{\{[5(1.507 - E)/0.059\,16] - 8\text{ pH}\}}$$

First analyte: $UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \quad E^\circ = 0.273\text{ V}$

$$\alpha_1 = 10^{\{2(0.273 - E)/0.059\,16 - 4\text{ pH}\}}$$

Second analyte: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\circ = 0.767\text{ V}$

$$\alpha_2 = 10^{(0.767 - E)/0.059\,16}$$

(a) First reaction: $2MnO_4^- + 5U^{4+} + 2H_2O \rightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+$

Second reaction: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(b) $$[U^{4+}] = \frac{5}{2}\left(\frac{\text{mmol } MnO_4^-}{25.0\text{ mL}}\right) = \frac{5}{2}\left(\frac{12.73\text{ mL} \times 0.009\,87\text{ M}}{25.0\text{ mL}}\right) = 0.012\,5_6\text{ M}$$

$$[Fe^{2+}] = 5\left(\frac{\text{mmol } MnO_4^-}{25.0\text{ mL}}\right) = 5\left(\frac{(31.21\text{-}12.73)\text{ mL} \times 0.009\,87\text{ M}}{25.0\text{ mL}}\right) = 0.036\,4_8\text{ M}$$

(c) From the stoichiometry of the two reactions, we know that

$$[Mn^{2+}] = \frac{2}{5}[UO_2^{2+}] + \frac{1}{5}[Fe^{3+}]$$

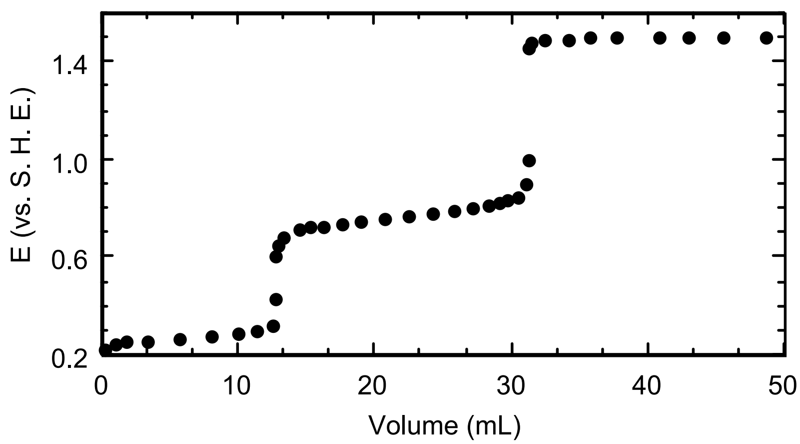
$$\frac{\tau Mn_{total}}{1+\tau} = \frac{2}{5}\frac{U_{total}}{1+\alpha_1} + \frac{1}{5}\frac{Fe_{total}}{1+\alpha_2}$$

$$\phi \equiv \frac{5}{2}\frac{Mn_{total}}{U_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{1}{1+\alpha_1} + \frac{1}{2}\frac{Fe_{total}/U_{total}}{1+\alpha_2}\right)$$

(d) Titration of U^{4+} + Fe^{2+} with permanganate

	A	B	C	D	E	F	G
1	E°(T) =	E (vs S.H.E.)	Tau	Alpha1	Alpha2	Phi	Volume(mL)
2	1.507	0.273	########	1.00E+00	2.24E+08	0.50000	6.365
3	E°(A1) =	0.434	4.86E+90	3.61E-06	4.25E+05	1.00000	12.730
4	0.273	0.767	3.49E+62	1.99E-17	1.00E+00	1.72575	21.969
5	E°(A2) =	1.458	1.38E+04	8.69E-41	2.09E-12	2.45168	31.210
6	0.767						
7	Nernst =						
8	0.05916		C2 = 10^(5*($A$2-B2)/$A$8-8*$A$12)				
9	Ve1 =		D2 = 10^(2*($A$4-B2)/$A$8-4*$A$12)				
10	12.73		E2 = 10^(($A$6-B2)/$A$8)				
11	pH =		F2 = ((1+C2)/C2)*((1/(1+D2))+((0.5*$A$14)/(1+E2)))				
12	0		G2 = $A$10*F2				
13	[Fe]/[U] =						
14	2.903						

(e)



G. (a) The analyte with the more negative reduction potential reacts first:

First: $2T + 3A \rightarrow 2T^{3-} + 3A^{2+}$ $E° = 0.93 - (-0.13) = 1.06$ V

$K = 10^{nE°/0.059\,16} = 10^{6(1.06)/0.059\,16} = 10^{107}$

Second: $T + 3B \rightarrow T^{3-} + 3B^{+}$ $E° = 0.93 - 0.46 = 0.47$ V

$K = 10^{nE°/0.059\,16} = 10^{3(0.57)/0.059\,16} = 10^{28}$

(b) 1*st*: $(100.0 \text{ mL})(0.300 \text{ M}) = \frac{3}{2} V_{e1} (1.00 \text{ M}) \Rightarrow V_{e1} = 20.0$ mL

2*nd*: $(100.0 \text{ mL})(0.060\,0 \text{ M}) = 3\,\Delta V (1.00 \text{ M}) \Rightarrow \Delta V = 2.00$ mL

$\Rightarrow V_{e2} = 22.0$ mL

(c) $\tau = \frac{[T^{3-}]}{[T]} \Rightarrow [T^{3-}] = \frac{\tau T_{total}}{1 + \tau}$

$\alpha = \frac{[A]}{[A^{2+}]} \Rightarrow [A^{2+}] = \frac{A_{total}}{1 + \alpha}$; $\beta = \frac{[B]}{[B^{+}]} \Rightarrow [B^{+}] = \frac{B_{total}}{1 + \beta}$

From the stoichiometry of the two titration reactions, we can say

$[T^{3-}] = \frac{2}{3} [A^{2+}] + \frac{1}{3} [B^{+}]$

$$\frac{\tau T_{total}}{1+\tau} = \frac{2}{3}\frac{A_{total}}{1+\alpha} + \frac{1}{3}\frac{B_{total}}{1+\beta}$$

From the stoichiometry of the first titration reaction, we define the fraction of titration as $\phi = (3/2)\ T_{total}/A_{total}$, because ϕ must be unity at V_{e1}.

Rearranging

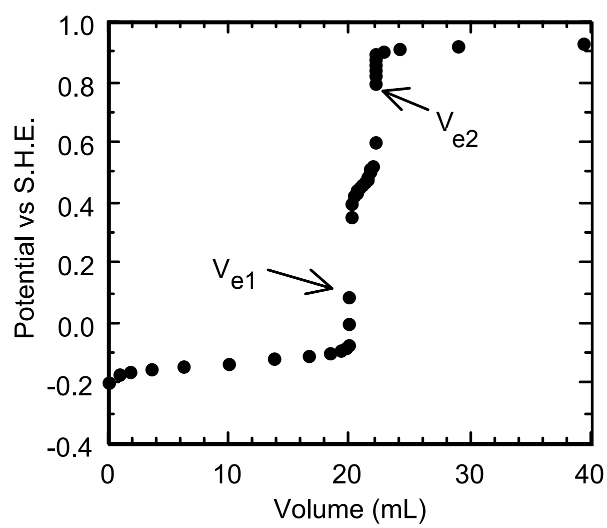
the equation above gives

$$\frac{T_{total}}{A_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{2}{3}\frac{1}{1+\alpha} + \frac{1}{3}\frac{B_{total}/A_{total}}{1+\beta}\right)$$

$$\phi = \frac{3}{2}\frac{T_{total}}{A_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{1}{1+\alpha} + \frac{1}{2}\frac{B_{total}/A_{total}}{1+\beta}\right)$$

(d) Titration of analytes A and B by titrant T

	A	B	C	D	E	F	G
1	E°(T) =	E (S.H.E.)	Tau	Alpha	Beta	Phi	Volume
2	0.93	-0.16	1.9E+55	1.0E+01	3.0E+10	0.08824	1.765
3	E°(A) =	-0.13	5.7E+53	1.0E+00	9.4E+09	0.50000	10.000
4	-0.13	-0.10	1.7E+52	9.7E-02	2.9E+09	0.91176	18.235
5	E°(B) =	0.086	6.3E+42	5.0E-08	2.1E+06	1.00000	20.000
6	0.46	0.43	2.3E+25	1.2E-19	3.2E+00	1.02373	20.475
7	Nernst =	0.46	6.8E+23	1.1E-20	1.0E+00	1.05000	21.000
8	0.05916	0.49	2.1E+22	1.1E-21	3.1E-01	1.07627	21.525
9	Ve1 =	0.797	5.6E+06	4.6E-32	2.0E-06	1.10000	22.000
10	20	0.9	3.3E+01	1.5E-35	3.7E-08	1.13312	22.662
11	[B]/[A] =						
12	0.2		C2 = 10^(3*($A$2-B2)/$A$8)				
13			D2 = 10^(2*($A$4-B2)/$A$8)				
14			E2 = 10^(($A$6-B2)/$A$8)				
15		F2 = ((1+C2)/C2)*((1/(1+D2))+((0.5*$A$14)/(1+E2)))					
16			G2 = $A$10*F2				



(e) E at V_{e1} = 0.086 V; E at V_{e2} = 0.797 V

H. First reaction: $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

Second reaction: $Ce^{4+} + Fe(phen)_3^{2+} \rightarrow Ce^{3+} + Fe(phen)_3^{3+}$

V_{e1} = 200.0 mL and V_{e2} = 200.1 mL

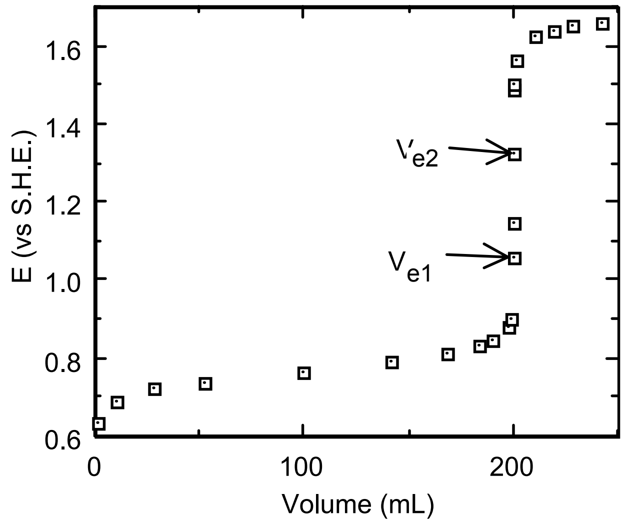
This problem is analogous to the titration of a mixture in Section 16-3, but the stoichiometry is 1:1:1 instead of 1:2:2. Equation 16-26 becomes $[Ce^{3+}] = [Fe^{3+}] + [Fe(phen)_3^{3+}]$ and Equation 16-27 becomes

$$\phi \equiv \frac{Ce_{total}}{Fe_{total}} = \left(\frac{1+\tau}{\tau}\right)\left(\frac{1}{1+\alpha_1} + \frac{Indictor_{total}/Fe_{total}}{1+\alpha_2}\right)$$

where α_1 applies to Fe^{2+} and α_2 applies to $Fe(phen)_3^{2+}$ (indicator) . The spreadsheet and graph below show that ferroin is excellent for this titration.

Spreadsheet for titration of $Fe^{2+} + Fe(phen)_3^{2+}$ with Ce^{4+}

	A	B	C	D	E	F	G
1	E°(T) =	E (S.H.E.)	Tau	Alpha1	Alpha2	Phi	Volume
2	1.7	0.631	1.2E+18	2.0E+02	5.3E+08	0.00500	1.000
3	E°(A) =	0.691	1.1E+17	1.9E+01	5.1E+07	0.04936	9.872
4	0.767	0.767	5.9E+15	1.0E+00	2.7E+06	0.50000	100.000
5	E°(B) =	0.843	3.1E+14	5.2E-02	1.4E+05	0.95064	190.128
6	1.147	0.903	3.0E+13	5.0E-03	1.3E+04	0.99500	199.000
7	Nernst =	1.055	8.0E+10	1.4E-05	3.6E+01	1.00000	200.000
8	0.05916	1.147	2.2E+09	3.8E-07	1.0E+00	1.00025	200.050
9	Ve1 =	1.326	2.1E+06	3.6E-10	9.4E-04	1.00050	200.100
10	200	1.487	4.0E+03	6.8E-13	1.8E-06	1.00075	200.150
11	[B]/[A] =	1.505	2.0E+03	3.4E-13	8.9E-07	1.00101	200.201
12	0.0005	1.561	2.2E+02	3.8E-14	1.0E-07	1.00497	200.995
13		1.623	2.0E+01	3.4E-15	9.0E-09	1.05046	210.093
14							
15	C2 = 10^(($A$2-B2)/$A$8)				E2 = 10^(($A$6-B2)/$A$8)		
16	D2 = 10^(($A$4-B2)/$A$8)				G2 = $A$10*F2		
17	F2 = ((1+C2)/C2)*(1/(1+D2)+$A$12/(1+E2))						



I. Titration of Fe^{2+} with dichromate

	A	B	C	D	E	F	G
1	E°(T) =	E(vs S.H.E.)	Tau	Alpha	Phi	E(vs Ag|AgCl)	Volume (mL)
2	1.36	0.653	5.06E+57	9.88E+01	0.01002	0.456	0.100
3	E°(A) =	0.735	2.44E+49	4.06E+00	0.19763	0.538	1.976
4	0.771	0.761	5.63E+46	1.48E+00	0.40391	0.564	4.039
5	Nernst =	0.781	5.27E+44	6.78E-01	0.59609	0.584	5.961
6	0.05916	0.807	1.22E+42	2.46E-01	0.80237	0.610	8.024
7	Ve =	0.827	1.14E+40	1.13E-01	0.89840	0.630	8.984
8	10	0.889	5.87E+33	1.01E-02	0.98998	0.692	9.900
9	pH =	1.177	3.63E+04	1.37E-07	1.00000	0.980	10.000
10	1	1.224	6.21E-01	2.20E-08	1.00990	1.027	10.099
11	V(Fe) =	1.234	6.01E-02	1.49E-08	1.10159	1.037	11.016
12	120	1.237	2.98E-02	1.33E-08	1.20313	1.040	12.031
13	[Cr]o =						
14	0.04		C2 = 10^(6*($A$2-B2)/$A$6-14*$A$10)				
15			D2 = 10^(($A$4-B2)/$A$6)				
16			E2 = (0.5+Sqrt(0.25+2*E2*$A$8*$A$14/				
17				(C2*E2*$A$8+C2*$A$12)))/(1+D2)			
18			F2 = B2-0.197				
19			G2 = $A$8*E2				