Chemical Equations for Multireaction Systems

Mei-Wen Yen

Department of Chemistry, Fordham University, Bronx, NY 10458, yen@murray.fordham.edu

Abstract: Algebraic equations were derived for plotting theoretical titration curves involving argentometric titration of binary halide mixtures. These generic equations are applied to three cases of binary halide mixtures in spreadsheet programs. The results are presented graphically as plots of half-cell potential versus volume of the titrant. This approach may serve as a more effective and logical method of showing students how to simulate a complex system involving multiple equilibria.

Introduction

To show students what transpires during a titration process, many analytical chemistry textbooks [1–5] present titration curves in detail. The major task is to unveil a unique property of the titration medium during the entire titration process. Away from the equivalence point the concentration of the titrant in the titration medium does not vary much; whereas, near the equivalence point it changes drastically. The detection of the equivalence point is, therefore, possible by choosing an indicator or a probe that reflects this unique change in concentration of the titrant.

While such an analysis may easily be accepted by students in cases involving a single analyte, it is often intimidating when a binary system, that is a system containing two analytes, is under discussion. As analytical chemistry textbooks [6, 7] often discuss multiple equilibria in depth, it is conceivable that one can extend this knowledge and apply it to the analysis of binary analyte systems.

Due to advancements in computer hardware and software technologies, utilization of spreadsheet programs in teaching analytical chemistry has become a trend in many textbooks. By using a spreadsheet program, many tedious and repetitive algebraic calculations can be performed by a computer within seconds. With this burden removed, both teachers and students can focus on the underlying chemical principles. Furthermore, it is also easy to present the results graphically to enhance students' learning through visual experience. One textbook [8] shows students how to derive equations based on mass-balance equations and solubility constants to construct the titration curve of a mixture of chloride and iodide titrated with a standard silver nitrate solution. The example is a good one; however, the approach is somewhat different from an experimenter's perspective. In a volumetric titration, the experimenter controls only two variables, namely, the concentration and added volume of the titrant. The former is established when the standard solution is prepared before the titration process starts. This leaves only one variable, the volume of the titrant, that can be controlled by the experimenter. It would be more realistic, therefore, to approach the problem from the question of "what changes are caused by the addition of a specific amount of the titrant ($AgNO_3$ solution) in an argentometric precipitation titration?" The answer is the equilibrium concentrations of $Ag^+(aq)$ and the two halide ions, after each addition of a specific amount of the $AgNO_3(aq)$ titrant. Once the problem is analyzed and understood, one may start solving it.

Discussion

Dividing the Titration Curve into Two Regions. A closer look at an argentometric titration of a binary halide mixture reveals the existence of two different regions. Initially, only the halide ion with the smaller solubility product will precipitate when $Ag^+(aq)$ is added. The second halide ion begins to precipitate with $Ag^+(aq)$ only after the concentration of the first halide ion decreases to a value where the second halide ion becomes competitive. It is apparent that conditions governing these two regions are quite different. At the initial stage, only one solubility equilibrium is involved; whereas, there are two solubility equilibria to be considered during the rest of the titration. It is imperative, therefore, to find the dividing line.

Before getting into the mathematics in detail, a few notations and terms need to be defined. These are listed below.

A = the molar concentration of the prepared standard $AgNO_3(aq)$
X = the molar concentration of the analyte $X^-(aq)$ in the original mixture
Y = the molar concentration of the analyte $Y^-(aq)$ in the original mixture
A' = the fictitious molar concentration of $Ag^+(aq)$
X' = the fictitious molar concentration of the analyte $X^-(aq)$
Y' = the fictitious molar concentration of the analyte $Y^-(aq)$
δA = the molar concentration of $Ag^+(aq)$ arising form dissolution of $AgY(s)$
$[Ag^+]$ = the equilibrium molar concentration of $Ag^+(aq)$
$[X^-]$ = the equilibrium molar concentration of the analyte $X^-(aq)$
$[Y^-]$ = the equilibrium molar concentration of the analyte $Y^-(aq)$
$K_1 = K_{sp}(AgX)$
$K_2 = K_{sp}(AgY)$

We also use AgX to represent the more soluble precipitate and AgY the less soluble one such that $K_1 > K_2$. The term "fictitious concentration" (i.e., A', X', and Y') refers to the calculated concentration of either Ag^+ or halide if no precipitation reactions were to occur. Because the same equilibrium condition may be attained through various routes, using these "fictitious concentrations" as the initial condition makes the calculations easier.

Table 1. Stoichiometric Analysis of the Solubility Equilibrium (2e)

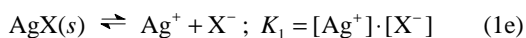|	Ag^+	+	Y^-	$\rightleftharpoons$	$AgY(s)$
Original:	A		Y		--
If no reaction after mixing:	A'		Y'		--
Changes due to reaction:	$- y$		$- y$		+ Solid
Equilibrium:	$A' - y$		$Y' - y$		Solid

Where Is the Dividing Line? There are two possible precipitation reactions. The first precipitation reaction involves analyte X^- and titrant Ag^+:

$$Ag^+ + X^- \rightleftharpoons AgX(s) ; \tag{1}$$
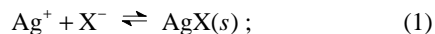
whereas, the second precipitation reaction involves analyte Y^- and the titrant Ag^+.

$$Ag^+ + Y^- \rightleftharpoons AgY(s) . \tag{2}$$
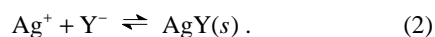
Hence, two corresponding solubility equilibria are under consideration are:

$$AgX(s) \rightleftharpoons Ag^+ + X^- ; \ K_1 = [Ag^+] \cdot [X^-] \tag{1e}$$

and

$$AgY(s) \rightleftharpoons Ag^+ + Y^- ; \ K_2 = [Ag^+] \cdot [Y^-] . \tag{2e}$$

Once all terms are defined, the first task is to find the dividing line. This does not seem difficult because the solubility products are known. Because $K_1 > K_2$, initially only the second precipitation reaction takes place. The analyte X^- will not precipitate until the reaction quotient exceeds its corresponding solubility product K_1.

Region I: $\left\{ [(A' - Y') + \delta A] \cdot X' < K_1 \right\}$, only the second equilibrium is present.

Region II: $\left\{ [(A' - Y') + \delta A] \cdot X' \geq K_1 \right\}$, both equilibria (1e) and (2e) coexist.

The term inside the square brackets represents the remaining Ag^+ concentration if only the second equilibrium is attained, and it consists of two terms. The first term, $(A' - Y')$, corresponds to the concentration of the excess Ag^+ if the second precipitation reaction is complete. The second term, δA, corrects for the slight incompleteness of this precipitation reaction. The exact answer to the condition will become apparent after a detailed analysis of region I.

Region I: Presence of the Solubility Equilibrium (2e) Only. Before analyte X^- becomes competitive, the only reaction occurring in the titration medium is the precipitation reaction between Ag^+ and analyte Y^-, namely reaction 2. Under this condition, equilibrium concentrations for all the species involved can be derived according to the stoichiometry set forth by the chemical equation (see Table 1).

The entries headed "Equilibrium" are derived equilibrium concentrations based upon the assumption that an amount y of Ag^+ and of Y^- are consumed before reaching equilibrium. To satisfy the equilibrium condition, the reaction quotient of the reverse reaction must equal the solubility product, that is

$$(A' - y) \cdot (Y' - y) = K_2 . \tag{3}$$

The above equation can be expanded and rearranged to a quadratic equation in y.

$$y^2 - (A' + Y')y + (A'Y' - K_2) = 0 \tag{4}$$

The only logical solution to this equation is determined based upon existing chemical information of the system.

$$y = \frac{(A' + Y') - \sqrt{(A' - Y')^2 + 4K_2}}{2} \tag{5}$$

Once y is determined, the equilibrium concentrations of all the relevant species can be found.

$$\text{Titrant } Ag^+: \ [Ag^+] = A' - y \tag{6}$$

$$\text{Analyte } X^-: \ [X^-] = X' \tag{7}$$

$$\text{Analyte } Y^-: \ [Y^-] = Y' - y \tag{8}$$

The Dividing Line, an Exact Answer. As discussed previously, to find the condition of the dividing line one needs to examine whether the reaction quotient of AgX exceeds its solubility product after the second solubility equilibrium has been reached. Under this specific circumstance, the aforementioned term inside the square brackets equals $(A' - y)$ and condition can be worked out as follows.

Region I, $\left[\dfrac{(A' - Y') + \sqrt{(A' - Y')^2 + 4K_2}}{2} \cdot X' \right] < K_1$:   only equilibrium (2e) is present.

Region II, $\left[\dfrac{(A' - Y') + \sqrt{(A' - Y')^2 + 4K_2}}{2} \cdot X' \right] \geq K_1$:   both equilibria (1e) and (2e) coexist.

Region II: Presence of Both Solubility Equilibria, (1e) and (2e). As the titration proceeds further, the analyte X^- eventually starts to compete against the analyte Y^- for the added Ag^+, and two solubility equilibria coexist. The equilibrium concentrations of all species involved can be derived based on the stoichiometry of both precipitation reactions (see Table 2).

The entries headed "Equilibrium" are derived equilibrium concentrations based on the assumption that x of analyte X^-, y of analyte Y^-, and thus $(x + y)$ of Ag^+ are consumed before reaching equilibrium. To satisfy both solubility equilibria, the following two algebraic equations exist.

$$[A' - (x + y)] \cdot (X' - x) = K_1 \tag{9}$$

Table 2. Stoichiometric Analysis of Two Co-existing Equilibria, (1e) and (2e)

	AgY(s) $\rightleftharpoons$	X$^-$	+	Ag$^+$	+	Y$^-$	$\rightleftharpoons$	AgY(s)
Original:	--	X		A		Y		--
If no reaction after mixing:	--	X'		A'		Y'		--
Changes due to reaction:	+ Solid	- x		- $(x+y)$		- y		+ Solid
Equilibrium:	Solid	$X'-x$		$A'-(x+y)$		$Y'-y$		Solid
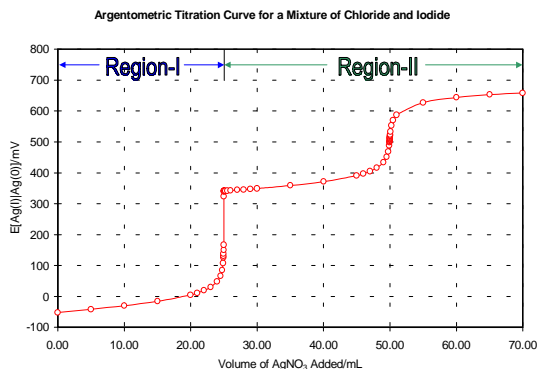
Figure 1. Calculated argentometric titration curve of a mixture of chloride and iodide, using the equations derived in this article. Concentrations of chloride, iodide, and the titrant (silver nitrate) are exactly 0.02000 M. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of AGNO$_3$ added. Region I starts from X = 0.00 ML and ends where the titration curve shows an abrupt change around the first equivalence point. Region II covers the rest of the titration.

$$[A'-(x+y)]\cdot(Y'-y) = K_2 \qquad (10)$$

Expanding and rearranging the sum of equations (9) and (10), a quadratic equation in $(x+y)$ is obtained.

$$(x+y)^2 - (A'+X'+Y')(x+y) + (A'X'+A'Y'-K_1-K_2) = 0 \qquad (11)$$

The only logical root of $(x+y)$ for the above equation is thus obtained through careful evaluation of the titration medium.

$$(x+y) = \frac{(A'+X'+Y') - \sqrt{(A'-X'-Y')^2+4K_1+4K_2}}{2} \qquad (12)$$

Dividing equation (9) by equation (10) and rearranging the resulting quotient yields another equation that describes the relationship between x and y.

$$x = \left(\frac{K_1}{K_2}\cdot y\right) - \left(\frac{K_1}{K_2}\cdot Y'\right) + X' \qquad (13)$$

From equations (12) and (13), y can be obtained directly, and x is simply the difference between equations (12) and (13).

$$y = \frac{\dfrac{(A'+X'+Y') - \sqrt{(A'-X'-Y')^2+4K_1+4K_2}}{2} + \left(\dfrac{K_1}{K_2}\cdot Y'\right) - X'}{\dfrac{K_1}{K_2}+1} \qquad (14)$$

Upon solving for x and y, the equilibrium concentrations of all relevant species are readily obtained.

$$\text{Titrant Ag}^+: \ \ [\text{Ag}^+] = A'-(x+y) \qquad (15)$$

$$\text{Analyte X}^-: \ \ [\text{X}^-] = X'-x \qquad (16)$$

$$\text{Analyte Y}^-: \ \ [\text{Y}^-] = Y'-y \qquad (17)$$

When a metallic silver electrode is used to probe the concentration of Ag$^+$ in the titration medium, its half-cell reaction and potential (at 25 °C) are given as follows.

$$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s); \ E° = 0.799 \ V \qquad (18)$$

$$E = E° + \left(0.05916 \ V\cdot\log[\text{Ag}^+]\right) \qquad (19)$$

Data

Equations derived from the Discussion section were used in Microsoft EXCEL$^®$ to calculate the necessary data points for each theoretical titration curve. Figures 1 through 3 show three sets of titration curves for cases where the concentrations of Ag$^+$, Cl$^-$, and I$^-$ are exactly 0.02000 M. Students may, at first, assume an approximation by considering only one single equilibrium at a time. Figures 4 through 6 show calculated titration curves based upon this approach under the same conditions. Due to the large difference (2×10^6 times) in solubility constants for AgCl and AgI, the two calculated titration curves for the mixture of Cl$^-$ and I$^-$ (Figure 1 versus Figure 4) do not show any significant difference, whether or not the second equilibrium is taken into consideration. As the difference in solubility constants becomes smaller, aberration begins to appear. The spikes around the equivalence points shown in Figures 5 and 6 are aberrations caused by neglecting the existence of the other solubility equilibrium in each case. Closely examining the data on the spreadsheets reveals the nature of these aberrations. In the mixture of bromide and iodide, bromide ions begin to precipitate with Ag$^+$ just a little before reaching the equivalence point of AgI. This coprecipitation phenomenon is easily explained by a difference of about six thousand times in the solubility products of AgBr and AgI. The titration error attributed to the coprecipitation is less than one percent in this case. In the mixture of chloride
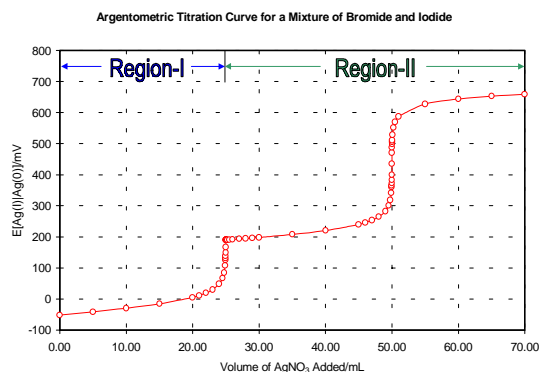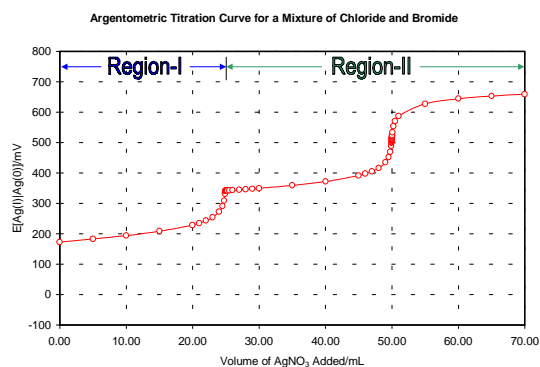
Figure 2. Calculated argentometric titration curve of a mixture of bromide and iodide, using the equations derived in this article. Concentrations of bromide, iodide, and the titrant (silver nitrate) are 0.02000 M exactly. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of $AGNO_3$ added. Region I starts from $X = 0.00$ ML and ends where the titration curve shows an abrupt change around the first equivalence point. Region II covers the rest of the titration.
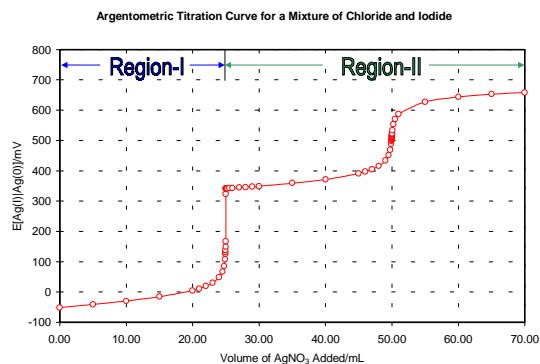

Figure 3. Calculated argentometric titration curve of a mixture of chloride and bromide, using the equations derived in this article. Concentrations of both analytes (chloride and bromide), as well as silver nitrate are exactly 0.02000 M. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of $AGNO_3$ added. Region I starts from $X = 0.00$ ML and ends where the titration curve shows an abrupt change around the first equivalence point. Region II covers the rest of the titration.

Figure 4. Calculated argentometric titration curve for a mixture of chloride and iodide if only one single precipitation reaction is considered in each region. Concentrations of both chloride and iodide are 0.02000 M as is that of silver nitrate. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of $AGNO_3$ added.
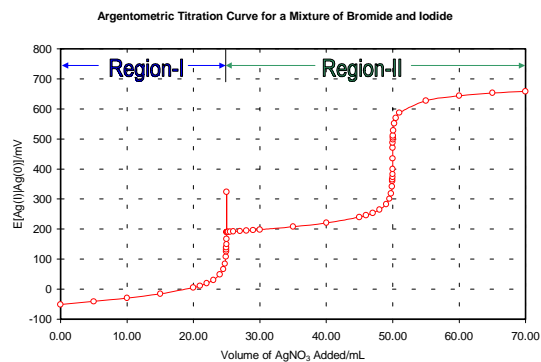

Figure 5. Calculated argentometric titration curve of a mixture of bromide and iodide if only one single precipitation reaction is considered in each region. Concentrations of both bromide and iodide are exactly 0.02000 M as is that of silver nitrate. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of $AGNO_3$ added.
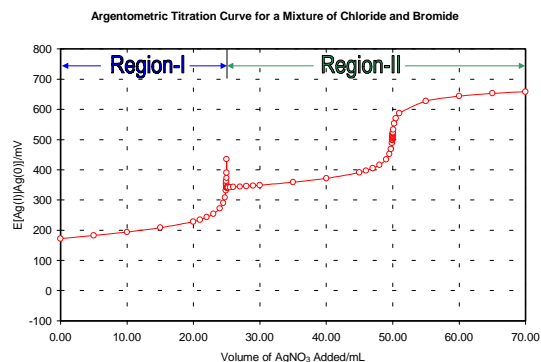

Figure 6. Calculated argentometric titration curve of a mixture of chloride and bromide if only one single precipitation reaction is considered in each region. Concentrations of both chloride and bromide are 0.02000 M as is that of silver nitrate. The half-cell potential (at 25 °C) of a silver indicator electrode is plotted against the volume of $AGNO_3$ added.

and bromide, chloride ions begin to precipitate with Ag^+ much before reaching the equivalence point of AgBr. Again, this coprecipitation phenomenon is easily rationalized with a difference of less than four hundred times in the solubility products of AgCl and AgBr. A titration error of two percent may be attributed to this coprecipitation phenomenon.

It is hoped that students may gain better understanding of the titration curve through this spreadsheet exercise. In addition, this also may serve as a model to show students how to tackle a complicated chemistry problem using rather simple algebra.

References

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