

Systematic Approach To Calculate the Concentration of Chemical Species in Multi-Equilibrium Problems

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The numerical calculation of chemical equilibrium problems is a basic skill needed by chemistry students and is of great value in a wide range of areas related to chemistry. It has attracted much attention since the 1950s when programmable computers became available. In the general approach, a set of simultaneous equations consisting of the equilibrium expressions, mass balances, and other balances, such as the charge balance and the balance for the reaction products, is solved (1–4). The particularities of each equilibria (e.g., acid–base, complexation, precipitation, and redox) usually give rise to different treatments for different equilibria (5). Solving simultaneous chemical equilibria of different types is not simple (6–13) unless some restrictions are established, such as fixing the pH or assuming the addition of an excess of complex reagent, as in the so-called Ringbom approach (14). In most cases, the complex mathematical treatment is demanding. We propose a systematic approach to calculate the concentration of the chemical species in multi-equilibrium systems. We demonstrate a simple way of implementing such calculations with the aid of a spreadsheet analysis tool.

Establishment of Balances Involving Chemical Species at Equilibrium

The systematic approach is based on the establishment of different balances involving the chemical species at equilibrium. Basically, three balances can be set up: (i) mass, (ii) charge, and (iii) stoichiometric balance for the reaction products.

Mass Balance

For each element or group of elements that remains unaltered during the reaction (e.g., acetate or sulfate ions), the mass balance can be written as

$$\sum_{j=1}^{N_0} \nu_j C_j = \sum_{i=1}^N \nu_i [A_i] \quad (1)$$

where N_0 is the number of chemical compounds containing the A element or group of elements that is added to the solution, N the number of species at equilibrium, ν_j and ν_i are the stoichiometric coefficients for A in each j chemical compound and i species, respectively, C_j is the concentration of each chemical compound before initiating the reaction, and $[A_i]$ is the concentration of each i species at equilibrium. Thus, the mass balance for silver ion in a mixture of AgNO_3 and ammonia, which gives rise to two ammine silver(I) ion complexes, is

$$C_{\text{AgNO}_3} = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+] \quad (2)$$

where C_{AgNO_3} is the concentration of dissolved AgNO_3 or the total concentration of silver in the solution as AgNO_3 is a strong electrolyte and will be fully dissociated. For ammonia, the mass balance is

$$C_{\text{NH}_3} = [\text{NH}_3] + [\text{NH}_4^+] + [\text{Ag}(\text{NH}_3)^+] + 2[\text{Ag}(\text{NH}_3)_2^+] \quad (3)$$

Both mass balances in eqs 2 and 3 are rather simple. Other more complex balances can be found. For example, for chromium added as potassium dichromate to an aqueous solution:

$$2C_{\text{K}_2\text{Cr}_2\text{O}_7} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + [\text{H}_2\text{CrO}_4] + 2[\text{Cr}_2\text{O}_7^{2-}] \quad (4)$$

and for acetate in a mixture of acetic acid (HAc), sodium acetate (NaAc), and copper acetate ($\text{Cu}(\text{Ac})_2$) in aqueous solution:

$$C_{\text{HAc}} + C_{\text{NaAc}} + 2C_{\text{Cu}(\text{Ac})_2} = [\text{HAc}] + [\text{Ac}^-] + [\text{Cu}(\text{Ac})^+] + 2[\text{Cu}(\text{Ac})_2] + 3[\text{Cu}(\text{Ac})_3^-] + 4[\text{Cu}(\text{Ac})_4^{2-}] \quad (5)$$

Charge Balance

This balance describes the electroneutrality of a solution once the equilibrium is reached. It can be used in any case where the charge of the chemical species changes upon reaction. This is the case of the mixture of AgNO_3 and ammonia:

$$[\text{H}^+] + [\text{NH}_4^+] + [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+] = [\text{OH}^-] + [\text{NO}_3^-] \quad (6)$$

This is a simple balance, as all involved species have a single charge. Also, because

$$[\text{NO}_3^-] = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+] \quad (7)$$

and the charge for nitrate and silver ions does not change upon reaction, eq 6 can be reduced to

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] \quad (8)$$

The charge balances for the aqueous solution of potassium dichromate and for a mixture of acetic acid (HAc), sodium acetate (NaAc), and copper acetate ($\text{Cu}(\text{Ac})_2$) are the following:

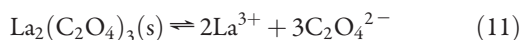
$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + 2[\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] \quad (9)$$

$$[\text{H}^+] + [\text{Na}^+] + 2[\text{Cu}^{2+}] + [\text{Cu}(\text{Ac})^+] \\ = [\text{OH}^-] + [\text{Ac}^-] + [\text{Cu}(\text{Ac})_3^-] + 2[\text{Cu}(\text{Ac})_4^{2-}] \quad (10)$$

The charge balance is used when there are ionic species for which the establishment of a mass balance is not easy, owing to the protagonism of the solvent. This is the case of H^+ and OH^- , when acid–base equilibria are involved.

Stoichiometric Balance for the Reaction Products

This balance can be set up for reactions involving two or more products that do not participate in other reactions. An example is



for which

$$[\text{La}^{3+}] = \frac{2}{3}[\text{C}_2\text{O}_4^{2-}] \quad (12)$$

Description of the Approach

The systematic approach is described using three examples.

Example 1: Formation of the Ammine Silver(I) Ion Complexes by Mixing AgNO_3 and NH_3

The formation of the ammine silver(I) ion complexes is used to describe the systematic approach. For this purpose, we consider a solution obtained by mixing AgNO_3 and ammonia to reach the concentrations $C_{\text{AgNO}_3} = 0.01 \text{ M}$ and $C_{\text{NH}_3} = 0.02 \text{ M}$. Four simultaneous equilibria take place: the formation of the two ammine silver(I) ion complexes, the hydrolysis of ammonia, and the self-ionization of water



where seven chemical species, Ag^+ , $\text{Ag}(\text{NH}_3)^+$, $\text{Ag}(\text{NH}_3)_2^+$, NH_3 , NH_4^+ , H^+ , and OH^- , participate. Note that the concentration of the NO_3^- ion will not change, at equilibrium: $[\text{NO}_3^-] = 0.01 \text{ M}$. In eqs 15 and 16, $\text{p}K_{\text{NH}_3} = -\log K_{\text{NH}_3}$ and $\text{p}K_w = -\log K_w$. The concentration of the seven species at equilibrium can be obtained by solving a system of seven equations containing the different species: the mass balances for silver and ammonia (eqs 2 and 3), the charge balance (eq 6 or alternatively, eq 8), and the following equations:

$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} \quad (17)$$

$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} \quad (18)$$

$$K_{\text{NH}_3} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (19)$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (20)$$

Owing to the nonlinearity of the equilibrium expressions, the most direct way of solving such a problem is minimizing the sum, χ , of squared null balances, b_k , involving the chemical species in the simultaneous reactions (i.e., searching the optimal combination of the unknowns that make $\chi \rightarrow 0$):

$$\chi = \sum_{k=1}^B (b_k)^2 \quad (21)$$

This allows a simple approach that can be tackled with the aid of a spreadsheet analysis tool, such as the Excel Solver. The number of b_k balances, B , included in eq 21 should be the difference between the involved chemical species, S , and the number of equilibrium reactions, R . In the example, there are seven species in solution and four reactions, therefore, $7 - 4 = 3$ balances are needed: eqs 2, 3, and 8 (or alternatively eq 6), which should be rewritten as

$$b_1 = C_{\text{AgNO}_3} - [\text{Ag}^+] - [\text{Ag}(\text{NH}_3)^+] - [\text{Ag}(\text{NH}_3)_2^+] \quad (22)$$

$$b_2 = C_{\text{NH}_3} - [\text{NH}_3] - [\text{NH}_4^+] - [\text{Ag}(\text{NH}_3)^+] \\ - 2[\text{Ag}(\text{NH}_3)_2^+] \quad (23)$$

$$b_3 = [\text{H}^+] + [\text{NH}_4^+] - [\text{OH}^-] \quad (24)$$

These balances will equal zero when the concentrations in brackets are those at equilibrium.

To solve the system of three equations (eqs 22–24), three unknowns should be selected. The most convenient ones for this example are $[\text{Ag}^+]$, $[\text{NH}_3]$, and $[\text{H}^+]$, which appear in two or more equilibria. The concentration of the other species coexisting in the solution, $\text{Ag}(\text{NH}_3)^+$, $\text{Ag}(\text{NH}_3)_2^+$, NH_4^+ , and OH^- , can be expressed as a function of the selected species through the four equilibrium expressions (eqs 17–20):

$$[\text{Ag}(\text{NH}_3)^+] = K_1[\text{Ag}^+][\text{NH}_3] \quad (25)$$

$$[\text{Ag}(\text{NH}_3)_2^+] = K_1K_2[\text{Ag}^+][\text{NH}_3]^2 \\ = K_2[\text{Ag}(\text{NH}_3)^+][\text{NH}_3] \quad (26)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad (27)$$

$$[\text{NH}_4^+] = K_{\text{NH}_3} \frac{[\text{NH}_3]}{[\text{OH}^-]} \quad (28)$$

The calculation process using a spreadsheet is depicted in Figure 1. The use of $\text{p}C = -\log C$ instead of C (C being the concentration of a chemical species selected as unknown) is essential for convergence in the Solver optimization process. This avoids negative values for the concentrations. The minimization should be initialized with a set of values (seeds). We used $\text{pAg} = 3$, $\text{pNH}_3 = 3$, and $\text{pH} = 7$, but other initial values can be also

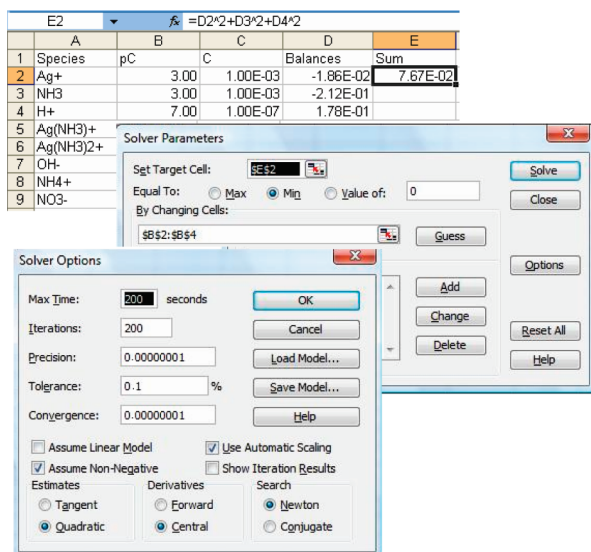


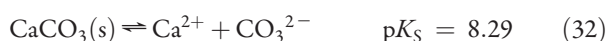
Figure 1. Calculation process for example 1, using the Solver option of the Excel spreadsheet.

adequate. It should be considered that convergence will be easier with seeds as close as possible to the solution. The concentration cells C5 to C8 (Figure 1) were calculated with eqs 25 to 28, respectively, according to the concentration of the unknowns (cells C2 to C4) and the equilibrium constants. The balances in cells D2 to D4 correspond to eqs 22 to 24 and were calculated with the values in cells C2 to C8. Finally, cell E2 includes the sum of squares (eq 21).

To increase the precision, when needed, the different balances should be weighted (i.e., multiplied by a factor of 10, 100, etc.) to increase their weight or reach similar magnitude. To improve the convergence, the parameters in the Excel Solver option were set as follows: maximal time (200 s), number of iterations (200), precision (10^{-8}), tolerance (0.1), convergence (10^{-8}), non-negative values, automatic scaling, quadratic estimation, central derivatives, and Newton search. The spreadsheet equations and the concentrations at equilibrium obtained with the Solver option are given in Figure 2. The flowchart in Figure 3 illustrates the whole calculation process.

Example 2: Solubility of Calcium Carbonate in Natural Waters

The systematic approach can be applied to any problem where several equilibria take place simultaneously, independently of the kind of reaction. We next examine a solution saturated with calcium carbonate and atmospheric CO_2 , without the addition of other reagent. The following reactions take place simultaneously:



Row	Column C	Column D	Column E
2	$=10^{\wedge}\text{-B2}$	$=0.01\text{-C2}\cdot\text{C5}\text{-C6}$	$=\text{D2}^{\wedge}2+\text{D3}^{\wedge}2+\text{D4}^{\wedge}2$
3	$=10^{\wedge}\text{-B3}$	$=0.02\text{-C3}\cdot\text{C8}\text{-C5}\cdot\text{C2}^{\wedge}2$	
4	$=10^{\wedge}\text{-B4}$	$=\text{C4}+\text{C8}\text{-C7}$	
5	$=(10^{\wedge}3.4)\cdot\text{C2}\cdot\text{C3}$		
6	$=(10^{\wedge}4)\cdot\text{C5}\cdot\text{C3}$		
7	$=(10^{\wedge}14)/\text{C4}$		
8	$=(10^{\wedge}4.75)\cdot\text{C3}/\text{C7}$		
9	$=0.01$		

E2		fx = D2*2+D3*2+D4*2			
	A	B	C	D	E
1	Species	pC	C	Balances	Sum
2	Ag+	3.58	2.65E-04	-7.04E-11	8.02E-21
3	NH3	2.94	1.16E-03	-5.41E-11	
4	H+	10.16	6.96E-11	1.17E-11	
5	Ag(NH3)+		7.73E-04		
6	Ag(NH3)2+		8.96E-03		
7	OH-		1.44E-04		
8	NH4+		1.44E-04		
9	NO3-		1.00E-02		

Figure 2. Spreadsheet equations for example 1 (see Figure 1) and concentrations at equilibrium obtained with Solver.

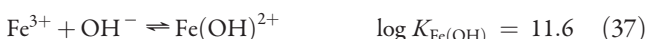
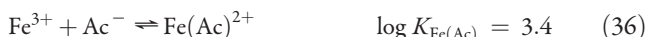
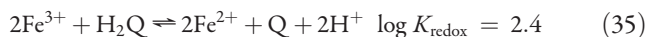
There are six chemical species in the aqueous solution, Ca^{2+} , CO_3^{2-} , HCO_3^- , H_2CO_3 , H^+ , and OH^- , and five reactions. Thus, only one balance with an unknown species is needed to solve the problem. In case of needing only one balance, the best option is the charge balance that involves species from the different equilibria and indicates the changes that take place in the solution:

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (34)$$

We chose $[\text{H}^+]$ (i.e., pH) as unknown, because it participates in several reactions; the concentrations of Ca^{2+} , CO_3^{2-} , HCO_3^- , H_2CO_3 , and OH^- were obtained from the equilibrium expressions for eqs 29–33. Note that $[\text{H}_2\text{CO}_3] = K_{\text{CO}_2} = 10^{-4.89} \text{ M}$ (7). The spreadsheet equations and the concentrations at equilibrium of all species in solution are shown in Figure 4.

Example 3: Reduction of Fe^{3+} by Hydroquinone in a Solution Containing Acetic Acid

We now consider a mixture of $\text{Fe}(\text{NO}_3)_3$, hydroquinone (H_2Q), and acetic acid (HAc), at concentrations $C_{\text{Fe}(\text{NO}_3)_3} = 0.02 \text{ M}$, $C_{\text{H}_2\text{Q}} = 0.02 \text{ M}$, and $C_{\text{HAc}} = 0.05 \text{ M}$. The iron(III) salt is fully dissociated in aqueous solution; therefore, the total concentration of the metal ion (the sum of all species at equilibrium containing iron, including $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$) will be $C_{\text{Fe}} = 0.02 \text{ M}$, also, $[\text{NO}_3^-] = 0.06 \text{ M}$. The redox reaction between Fe^{3+} and H_2Q is altered by complexation of the metal by the acetate ion (Ac^-), which in turn, is protonated in the acidic medium:



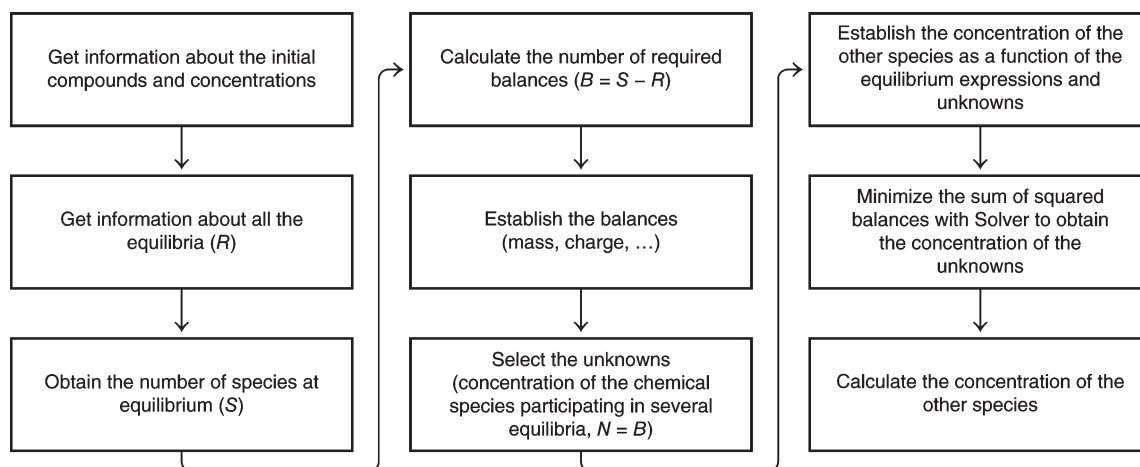


Figure 3. Flowchart indicating the steps of the systematic approach.

Row	Column C	Column D	Column E
2	=10^A-B2	=C2+2*C6-C7-2*C5-C4	=D2^2
3	=10^A-4.89		
4	=(10^A-6.35)*C3/C2		
5	=(10^A-10.33)*C4/C2		
6	=(10^A-8.29)/C5		
7	=(10^A-14)/C2		

E2		fx = D2^2			
	A	B	C	D	E
1	Species	pC		Balances	Sum
2	H+	8.27	5.36E-09	-2.49E-12	6.21E-24
3	H2CO3		1.29E-05		
4	HCO3-		1.07E-03		
5	CO32-		9.37E-06		
6	Ca2+		5.47E-04		
7	OH-		1.87E-06		

Figure 4. Spreadsheet equations for example 2 and concentrations at equilibrium obtained with Solver.

This is a complex example involving 10 species, Fe^{3+} , Fe^{2+} , $\text{Fe}(\text{Ac})^{2+}$, $\text{Fe}(\text{OH})^{2+}$, HAc , Ac^- , H_2Q , Q , H^+ , and OH^- , and only five reactions; therefore, five balances are needed: the three mass balances for the three systems involved in the reactions (eqs 40–42), the charge balance (eq 43), and the stoichiometric balance for the products in the redox reaction (eq 44):

$$C_{\text{Fe}} = [\text{Fe}^{3+}] + [\text{Fe}^{2+}] + [\text{Fe}(\text{Ac})^{2+}] + [\text{Fe}(\text{OH})^{2+}] \quad (40)$$

$$C_{\text{H}_2\text{Q}} = [\text{H}_2\text{Q}] + [\text{Q}] \quad (41)$$

$$C_{\text{HAc}} = [\text{Ac}^-] + [\text{HAc}] + [\text{Fe}(\text{Ac})^{2+}] \quad (42)$$

$$[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{Fe}(\text{Ac})^{2+}] + 2[\text{Fe}(\text{OH})^{2+}] + 2[\text{Fe}^{2+}] = [\text{OH}^-] + [\text{Ac}^-] + [\text{NO}_3^-] \quad (43)$$

$$[\text{Fe}^{2+}] = 2[\text{Q}] \quad (44)$$

Note that in this example, besides the mass balances and the charge balance, we need another type of balance to make explicit

Row	Column C	Column D	Column E
2	=10^A-B2	=0.02-C2-C7-C8-C9	=D2^2+D3^2+D4^2+D5^2
3	=10^A-B3	=0.02-C3-C11	
4	=10^A-B4	=0.05-C4-C10-C8	
5	=10^A-B5	=C5+3*C2+2*C8+2*C9+2*C7-C6-C4-C12	
6	=(10^A-14)/C5		
7	=2*C3		
8	=(10^3.4)*C2*C4		
9	=(10^11.6)*C2*C6		
10	=C4*C5/(10^4.78)		
11	=(C7^2)*C3*(C5^2)/(C2^2)*(10^2.4)		
12	=0.06		

E2		fx = D2^2+D3^2+D4^2+D5^2			
	A	B	C	D	E
1	Species	pC		Balances	Sum
2	Fe3+	4.60	2.52E-05	4.53E-11	3.58E-21
3	Q	2.00	9.98E-03	1.38E-11	
4	Ac-	4.36	4.34E-05	1.41E-11	
5	H+	1.70	2.00E-02	3.37E-11	
6	OH-		5.00E-13		
7	Fe2+		2.00E-02		
8	Fe(Ac)2+		2.74E-06		
9	Fe(OH)2+		5.01E-06		
10	HAc		5.00E-02		
11	H2Q		1.00E-02		
12	NO3-		6.00E-02		

Figure 5. Spreadsheet equations for example 3 and concentrations at equilibrium obtained with Solver.

the electron transfer processes. We propose here the use of the stoichiometric balance (eq 44).

To facilitate the computing process, we reduced, however, the number of balances to four (eqs 40–43), and selected the species Fe^{3+} , Ac^- , Q , and H^+ for the minimization process; $\text{Fe}(\text{Ac})^{2+}$, $\text{Fe}(\text{OH})^{2+}$, HAc , OH^- , H_2Q , and Fe^{2+} were expressed as functions of the selected unknowns using the equilibrium expressions for the reactions in eqs 36–39, eq 35, and eq 44. The spreadsheet equations and the concentrations at equilibrium are shown in Figure 5. It is also possible to calculate the concentrations of the chemical species when the pH is known. In that case, the χ function will not include the charge balance (eq 43), and the unknown species will be reduced to Fe^{3+} , Q , and Ac^- . This is useful to examine the dependence of the equilibrium on pH.

Conclusions

When two or more simultaneous reactions take place in an aqueous solution, a system of equations should be solved to calculate the concentration of each chemical species at equilibrium, which is particularly challenging for students with insufficient chemical and mathematical skills. The systematic approach suggested here simplifies this calculation, whatever the number of involved reactions or chemical species. There is no restriction in the type of reaction, only the equilibrium constants should be known.

The systematic approach is useful for cases where the pH is unknown or in any other situation where the Ringbom approach, based on the use of conditional constants, cannot be applied. However, in cases involving a large number of reactions where one or more experimental conditions are fixed, it can be convenient to combine previously two or more reactions, using the conditional constant of the main reaction instead.

Any powerful minimization algorithm can be used to solve the set of equations. In this work, we demonstrate that the Solver option in the Microsoft Excel spreadsheet, based on the nonlinear least-squares routine on the Levenberg–Marquardt algorithm (15, 16), can yield accurate results. Students with a basic knowledge of chemical reactions, of the calculation of the concentration of species at equilibrium, and of the Solver option of the Excel spreadsheet can carry out easily the entire process from start to finish. The approach allows instructors to highlight the importance of establishing balances in equilibrium problems without the obscuring factor of difficult mathematics.

The use of a systematic approach to solve the simultaneous equations that describe the equilibrium conditions is important, but if students are to understand equilibrium systems, they should be able to make reasonable approximations of the concentrations at equilibrium from starting conditions (e.g., initial concentrations and equilibrium constants). This also helps to provide good seeds to initialize the minimization process in the systematic approach.

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