Systems of Nonlinear Equations for Simultaneous Equilibria

Consider what happens when we add $m^0_{\mathrm{H_2C_2O_4}}$ moles of oxalic acid to 1 kg of pure water. The associated chemical equilibria are:

$$\begin{aligned} \mathrm{H_2C_2O_4}(aq) + \mathrm{H_2O} &\rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{HC_2O_4^-}(aq) & K_{a1} &= 5.6\cdot 10^{-2} \\ \mathrm{HC_2O_4^-}(aq) + \mathrm{H_2O} &\rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{C_2O_4^{2-}}(aq) & K_{a2} &= 1.5\cdot 10^{-4} \\ 2\mathrm{H_2O} &\rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) & K_w &= 10^{-14} \end{aligned} \tag{11.1}$$

and the different species involved can be expressed in terms of the progress of the chemical reactions as:

$$\begin{aligned} m_{\mathrm{H_2C_2O_4}} &= m^0_{\mathrm{H_2C_2O_4}} - \xi_{a1} \\ m_{\mathrm{HC_2O_4^-}} &= \xi_{a1} - \xi_{a2} \\ m_{\mathrm{C_2O_4^{-2}}} &= \xi_{a2} \\ m_{\mathrm{H_3O^+}} &= \xi_{a1} + \xi_{a2} + \xi_w \\ m_{\mathrm{OH^-}} &= \xi_w \end{aligned} \tag{11.2}$$

And so we have the following equilibrium equations:

$$\begin{aligned} K_{a1} &= \frac{(\xi_{a1} - \xi_{a2})(\xi_{a1} + \xi_{a2} + \xi_w)}{m^0_{\mathrm{H_2C_2O_4}} - \xi_{a1}} \\ K_{a2} &= \frac{\xi_{a2}(\xi_{a1} + \xi_{a2} + \xi_w)}{(\xi_{a1} - \xi_{a2})} \\ K_w &= \xi_w(\xi_{a1} + \xi_{a2} + \xi_w) \end{aligned} \tag{11.3}$$

Determining the progress of the reactions requires solving three *nonlinear* equations in three unknowns.

Let us rewrite the equations as:

$$\begin{aligned} 0 = f_1(\xi_{a1}, \xi_{a2}, \xi_w) &= K_{a1}\left(m^0_{\mathrm{H_2C_2O_4}} - \xi_{a1}\right) - (\xi_{a1} - \xi_{a2})(\xi_{a1} + \xi_{a2} + \xi_w) \\ 0 = f_2(\xi_{a1}, \xi_{a2}, \xi_w) &= K_{a_2}(\xi_{a1} - \xi_{a2}) - \xi_{a2}(\xi_{a1} + \xi_{a2} + \xi_w) \\ 0 = f_3(\xi_{a1}, \xi_{a2}, \xi_w) &= K_w - \xi_w(\xi_{a1} + \xi_{a2} + \xi_w) \end{aligned} \tag{11.4}$$

Suppose we had an initial guess for a solution, $\left\{\xi^{(0)}_{a1}, \xi^{(0)}_{a2}, \xi^{(0)}_w\right\}$. We could approximate the change in the value of the equations (11.4) due a change in the progresses of reactions as

$$df_k = \left(\frac{\partial f_k}{\partial \xi_{a1}}\right)_{\xi_{a2},\xi_w} d\xi_{a1} + \left(\frac{\partial f_k}{\partial \xi_{a2}}\right)_{\xi_{a1},\xi_w} d\xi_{a2} + \left(\frac{\partial f_k}{\partial \xi_w}\right)_{\xi_{a1},\xi_{a2}} d\xi_w \tag{11.5}$$

A small change in the values of the functions in Eq. (11.4) can then be written as:

$$\begin{bmatrix} \Delta f_1 \\ \Delta f_2 \\ \Delta f_3 \end{bmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial \xi_{a1}} & \dfrac{\partial f_1}{\partial \xi_{a2}} & \dfrac{\partial f_1}{\partial \xi_w} \\ \dfrac{\partial f_2}{\partial \xi_{a1}} & \dfrac{\partial f_2}{\partial \xi_{a2}} & \dfrac{\partial f_2}{\partial \xi_w} \\ \dfrac{\partial f_3}{\partial \xi_{a1}} & \dfrac{\partial f_3}{\partial \xi_{a2}} & \dfrac{\partial f_3}{\partial \xi_w} \end{bmatrix} \begin{bmatrix} \Delta \xi_{a1} \\ \Delta \xi_{a2} \\ \Delta \xi_w \end{bmatrix} \tag{11.6}$$

This suggests that from an initial guess, we can approximate the solution to the equations by

$$\begin{aligned} f_1\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) + \Delta f_1 = 0 \\ f_2\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) + \Delta f_2 = 0 \\ f_3\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) + \Delta f_3 = 0 \end{aligned} \tag{11.7}$$

or in matrix-vector notation, using Eq. (11.6),

$$\begin{bmatrix} -f_1\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) \\ -f_2\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) \\ -f_3\left(\xi_{a1}^{(0)}, \xi_{a2}^{(0)}, \xi_w^{(0)}\right) \end{bmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial \xi_{a1}} & \dfrac{\partial f_1}{\partial \xi_{a2}} & \dfrac{\partial f_1}{\partial \xi_w} \\ \dfrac{\partial f_2}{\partial \xi_{a1}} & \dfrac{\partial f_2}{\partial \xi_{a2}} & \dfrac{\partial f_2}{\partial \xi_w} \\ \dfrac{\partial f_3}{\partial \xi_{a1}} & \dfrac{\partial f_3}{\partial \xi_{a2}} & \dfrac{\partial f_3}{\partial \xi_w} \end{bmatrix} \begin{bmatrix} \Delta \xi_{a1} \\ \Delta \xi_{a2} \\ \Delta \xi_w \end{bmatrix} \tag{11.8}$$

This is a system of *linear* equations to solve that produces an improved guess for the solution, namely,

$$\begin{bmatrix} \xi_{a1}^{(1)} \\ \xi_{a2}^{(1)} \\ \xi_w^{(1)} \end{bmatrix} = \begin{bmatrix} \xi_{a1}^{(0)} \\ \xi_{a2}^{(0)} \\ \xi_w^{(0)} \end{bmatrix} + \begin{bmatrix} \Delta \xi_{a1} \\ \Delta \xi_{a2} \\ \Delta \xi_w \end{bmatrix} \tag{11.9}$$

This gives an improved estimate for the solution to the equations. We can reinsert this improved solution into Eq. (11.8), defining the iterative procedure that is called Newton's method for a system of nonlinear equations,

$$\begin{bmatrix} -f_1\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right) \\ -f_2\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right) \\ -f_3\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right) \end{bmatrix} = \begin{bmatrix} \frac{\partial f_1\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a1}} & \frac{\partial f_1\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a2}} & \frac{\partial f_1\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{w}} \\ \frac{\partial f_2\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a1}} & \frac{\partial f_2\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a2}} & \frac{\partial f_2\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{w}} \\ \frac{\partial f_3\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a1}} & \frac{\partial f_3\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{a2}} & \frac{\partial f_3\left(\xi_{a1}^{(k)},\xi_{a2}^{(k)},\xi_{w}^{(k)}\right)}{\partial \xi_{w}} \end{bmatrix} \begin{bmatrix} \Delta\xi_{a1} \\ \Delta\xi_{a2} \\ \Delta\xi_{w} \end{bmatrix}$$

$$\begin{bmatrix} \xi_{a1}^{(k+1)} \\ \xi_{a1}^{(k+1)} \\ \xi_{a1}^{(k+1)} \end{bmatrix} = \begin{bmatrix} \xi_{a1}^{(k)} \\ \xi_{a1}^{(k)} \\ \xi_{a1}^{(k)} \end{bmatrix} + \begin{bmatrix} \Delta\xi_{a1} \\ \Delta\xi_{a2} \\ \Delta\xi_{w} \end{bmatrix} \tag{11.10}$$

The matrix in this equation is called the *Jacobian* of the nonlinear system.

As a specific example, consider adding $1\cdot10^{-4}$ moles of oxalic acid to 1 kg of pure water. An initial guess can be obtained by treating this in the way one would in general chemistry, namely, treating the ionizations one-step at a time. So the first acid dissociation would be

$$\begin{aligned} 5.6\cdot10^{-2} &= \frac{\xi_{a1}^2}{10^{-4}-\xi_{a1}} \\ \xi_{a1}^2 - 5.6\cdot10^{-2}\left(10^{-4}-\xi_{a1}\right) &= 0 \\ \xi_{a1}^2 + 5.6\cdot10^{-2}\xi_{a1} - 5.6\cdot10^{-6} &= 0 \\ \xi_{a1} &= \frac{-5.6\cdot10^{-2} \pm \sqrt{\left(5.6\cdot10^{-2}\right)^2 + 4\left(5.6\cdot10^{-6}\right)}}{2} \\ &= 9.98\cdot10^{-5} \end{aligned} \tag{11.11}$$

and the second acid dissociation would be

$$\begin{aligned} 1.5\cdot10^{-4} &= \frac{\left(9.98\cdot10^{-5}+\xi_{a2}\right)\xi_{a2}}{9.98\cdot10^{-5}-\xi_{a2}} \\ 0 &= \xi_{a2}^2 + \left(9.98\cdot10^{-5}+1.5\cdot10^{-4}\right)\xi_{a2} - \left(1.5\cdot10^{-4}\right)\left(9.98\cdot10^{-5}\right) \\ \xi_{a2} &= 4.99\cdot10^{-5} \end{aligned} \tag{11.12}$$

And since the number of protons formed from acid dissociation is:

$$m_{\mathrm{H_3O^+}} \approx \xi_{a1} + \xi_{a2} = 9.98\cdot10^{-5} + 4.99\cdot10^{-5} = 1.5\cdot10^{-4} \tag{11.13}$$

and so

$$\begin{aligned} 10^{-14} &= \xi_w\left(1.5\cdot10^{-4}+\xi_w\right) \\ 0 &= \xi_w^2 + 1.5\cdot10^{-4}\xi_w - 10^{-14} \\ \xi_w &= 6.67\cdot10^{-11} \end{aligned} \tag{11.14}$$

Now, we evaluate the Jacobian of the system,

$$\begin{bmatrix} \frac{\partial f_1}{\partial \xi_{a1}} & \frac{\partial f_1}{\partial \xi_{a2}} & \frac{\partial f_1}{\partial \xi_w} \\ \frac{\partial f_2}{\partial \xi_{a1}} & \frac{\partial f_2}{\partial \xi_{a2}} & \frac{\partial f_2}{\partial \xi_w} \\ \frac{\partial f_3}{\partial \xi_{a1}} & \frac{\partial f_3}{\partial \xi_{a2}} & \frac{\partial f_3}{\partial \xi_w} \end{bmatrix} = \begin{bmatrix} -K_{a1} - 2\xi_{a1} - \xi_w & 2\xi_{a2} + \xi_w & -\xi_{a1} + \xi_{a2} \\ K_{a2} - \xi_{a2} & -K_{a2} - 2\xi_{a2} - \xi_{a1} - \xi_w & -\xi_{a2} \\ -\xi_w & -\xi_w & -\xi_{a1} - \xi_{a2} - 2\xi_w \end{bmatrix} \tag{11.15}$$

and we solve the following linear system,

$$\begin{bmatrix} -5.6 \cdot 10^{-2} & 9.98 \cdot 10^{-5} & -4.99 \cdot 10^{-5} \\ 1.001 \cdot 10^{-4} & -3.496 \cdot 10^{-4} & -4.99 \cdot 10^{-5} \\ -6.67 \cdot 10^{-11} & -6.67 \cdot 10^{-11} & -1.497 \cdot 10^{-4} \end{bmatrix} \begin{bmatrix} \Delta\xi_{a1} \\ \Delta\xi_{a2} \\ \Delta\xi_w \end{bmatrix} = -\begin{bmatrix} 3.72997 \cdot 10^{-9} \\ 1.49667 \cdot 10^{-11} \\ 1.50056 \cdot 10^{-17} \end{bmatrix} \tag{11.16}$$

obtaining

$$\begin{bmatrix} \Delta\xi_{a1} \\ \Delta\xi_{a2} \\ \Delta\xi_w \end{bmatrix} = \begin{bmatrix} 6.65 \cdot 10^{-8} \\ 6.18 \cdot 10^{-8} \\ 4.30 \cdot 10^{-14} \end{bmatrix} \tag{11.17}$$

Indicating that our initial guess was quite good. If it were not accurate enough, we would insert the corrected values from this iteration and resolve the procedure, repeating until sufficient accuracy was obtained.

In general, given a system of m nonlinear equations in m unknowns,

$$f_k\left(x_1, x_2, \ldots, x_m\right) = 0 \qquad k = 1, 2, \ldots m \tag{11.18}$$

with an initial guess, we can construct an improved solution by expanding f in a Taylor series,

$$f_k\left(x_1, x_2, \ldots x_m\right) = f_k\left(x_1^{\text{guess}}, x_2^{\text{guess}}, \ldots x_m^{\text{guess}}\right) + \sum_{j=1}^{m} \left(\frac{\partial f}{\partial x_j}\right)\left(x_j - x_j^{\text{guess}}\right) + \begin{pmatrix} \text{higher} \\ \text{order} \\ \text{terms} \end{pmatrix} \tag{11.19}$$

This means that an improved solution can be obtained by solving the linear system of equations

$$-\begin{bmatrix} f_1\left(x_1^{\text{guess}}, x_2^{\text{guess}}, \ldots x_m^{\text{guess}}\right) \\ f_2\left(x_1^{\text{guess}}, x_2^{\text{guess}}, \ldots x_m^{\text{guess}}\right) \\ \vdots \\ f_m\left(x_1^{\text{guess}}, x_2^{\text{guess}}, \ldots x_m^{\text{guess}}\right) \end{bmatrix} = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_m} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_m} \\ \vdots & \vdots & & \vdots \\ \frac{\partial f_m}{\partial x_1} & \frac{\partial f_m}{\partial x_2} & \cdots & \frac{\partial f_m}{\partial x_m} \end{bmatrix} \begin{bmatrix} x_1 - x_1^{\text{guess}} \\ x_2 - x_2^{\text{guess}} \\ \vdots \\ x_m - x_m^{\text{guess}} \end{bmatrix} \tag{11.20}$$

This is the "generic" form of Newton's method for systems of nonlinear equations. The matrix in this equation is called the Jacobian.

As a final example, let's consider what happens to a sparingly soluble salt of a weak acid. Specifically, we consider Scandium Fluoride, which is described by the reactions below:

$$
\begin{aligned}
\mathrm{ScF_3}(s) &\rightleftarrows \mathrm{Sc^{+3}}(aq) + 3\mathrm{F^-}(aq) & K_{sp} &= 4.2\cdot 10^{-18} \\
\mathrm{HF}(aq) + \mathrm{H_2O} &\rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) & K_a &= 5.6\cdot 10^{-4} \\
2\mathrm{H_2O} &\rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) & K_w &= 10^{-14}
\end{aligned}
\tag{11.21}
$$

The molality of the various species are given by:

$$
\begin{aligned}
m_{\mathrm{Sc^{+3}}} &= \xi_{sp} \\
m_{\mathrm{F^-}} &= 3\xi_{sp} + \xi_a \\
m_{\mathrm{HF}} &= -\xi_a \\
m_{\mathrm{H_3O^+}} &= \xi_a + \xi_w \\
m_{\mathrm{OH^-}} &= \xi_w
\end{aligned}
\tag{11.22}
$$

equilibrium equations are:

$$
\begin{aligned}
K_{sp} &= \xi_{sp}\left(3\xi_{sp} + \xi_a\right)^3 \\
K_a &= \frac{\left(3\xi_{sp} + \xi_a\right)\left(\xi_a + \xi_w\right)}{-\xi_a} \\
K_w &= \xi_w\left(\xi_a + \xi_w\right)
\end{aligned}
\tag{11.23}
$$

which can be rewritten as:

$$
\begin{aligned}
0 &= f_1\left(\xi_{sp},\xi_a,\xi_w\right) \equiv K_{sp} - \xi_{sp}\left(3\xi_{sp} + \xi_a\right)^3 \\
0 &= f_2\left(\xi_{sp},\xi_a,\xi_w\right) = \left(3\xi_{sp} + \xi_a\right)\left(\xi_a + \xi_w\right) + K_a\xi_a \\
0 &= f_3\left(\xi_{sp},\xi_a,\xi_w\right) = K_w - \xi_w\left(\xi_a + \xi_w\right)
\end{aligned}
\tag{11.24}
$$

The initial guess can be obtained by solving the "general chemistry" problem, ignoring the coupling between the reactions. In that case,

$$
\begin{aligned}
\xi_{sp}\left(3\xi_{sp}\right)^3 &= 4.2\cdot 10^{-18} \\
\xi_{sp} &= 1.99\cdot 10^{-5}
\end{aligned}
\tag{11.25}
$$

and for the acid dissociation,

$$
\begin{aligned}
\xi_a^2 + 3\xi_{sp}\xi_a + K_a\xi_a &= 0 \\
\xi_a &= -\left(K_a + 3\xi_{sp}\right) = -6.2\cdot 10^{-4}
\end{aligned}
\tag{11.26}
$$

and for the water dissociation

$$
\begin{aligned}
\xi_w^2 + \xi_w\xi_a - 10^{-14} &= 0 \\
\xi_w &= 6.2\cdot 10^{-4}
\end{aligned}
\tag{11.27}
$$

Then you solve the nonlinear system, with the Jacobian:

$$\begin{bmatrix} \frac{\partial f_1}{\partial \xi_{sp}} & \frac{\partial f_1}{\partial \xi_a} & \frac{\partial f_1}{\partial \xi_w} \\ \frac{\partial f_2}{\partial \xi_{sp}} & \frac{\partial f_2}{\partial \xi_a} & \frac{\partial f_2}{\partial \xi_w} \\ \frac{\partial f_3}{\partial \xi_{sp}} & \frac{\partial f_3}{\partial \xi_a} & \frac{\partial f_3}{\partial \xi_w} \end{bmatrix} = \begin{bmatrix} 108\xi_{sp}^3 & 3\xi_{sp}\left(3\xi_{sp}+\xi_a\right)^2 & 0 \\ 3\left(\xi_a+\xi_w\right) & K_a+3\xi_{sp}+2\xi_a+\xi_w & 3\xi_{sp}+\xi_a \\ 0 & -\xi_w & -\xi_a-2\xi_w \end{bmatrix} \tag{11.28}$$

Exercise:
Use Newton's method to solve the following equations. Use $x = 3$, $y = -1.5$ as your initial guess.

$$\begin{aligned} x+e^{-x}+y^3 &= 0 \\ x^2+2xy-y^2+\tan x &= 0 \end{aligned} \tag{11.29}$$

(answer: $x = 3.13$, $y = -1.47$)

Exercise:
A saturated solution of Calcium Oxalate is made in pure water. What is the pH of the solution? The key reactions and equilibrium constants are:

$$\begin{aligned} CaC_2O_4(s) &\rightleftarrows Ca^{+2}(aq)+C_2O_4^{2-}(aq) & K_{sp} &= 2.7\cdot 10^{-9} \\ H_2C_2O_4(aq)+H_2O &\rightleftarrows H_3O^{+}(aq)+HC_2O_4^{-}(aq) & K_{a1} &= 5.6\cdot 10^{-2} \\ HC_2O_4^{-}(aq)+H_2O &\rightleftarrows H_3O^{+}(aq)+C_2O_4^{2-}(aq) & K_{a2} &= 1.5\cdot 10^{-4} \\ 2H_2O &\rightleftarrows H_3O^{+}(aq)+OH^{-}(aq) & K_w &= 10^{-14} \end{aligned} \tag{11.30}$$

Extension:
When one dissolves carbon dioxide in water, as one does in carbonated beverages, the water becomes acidic. The key reactions are:

$$\begin{aligned} CO_2(g) &\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CO_2(aq) & K_p &= \frac{\left[CO_2(aq)\right]}{p_{CO_2}} = .0337\ \tfrac{\text{M}}{\text{atm}} \\ H_2O+CO_2(aq) &\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2CO_3(aq) & K_h &= 1.7\cdot 10^{-3} \\ H_2CO_3(aq) &\underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} H^{+}(aq)+HCO_3^{-}(aq) & K_1 &= 2.5\cdot 10^{-4} \\ HCO_3^{-}(aq) &\underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} H^{+}(aq)+CO_3^{2-}(aq) & K_2 &= 4.69\cdot 10^{-11} \end{aligned} \tag{11.31}$$

(a) assume that the partial pressure of carbon dioxide is 1 atm. What is the pH of the solution?
(b) the carbonated water container is left open to the atmosphere and it goes flat. the partial pressure of carbon dioxide it the atmosphere is x. What is the pH of the solution?

Exercise:
Consider the dissolution of citric acid in pure water. The key equations are

$$\begin{aligned} H_3C_6H_5O_7+H_2O &\rightarrow H_2C_6H_5O_7^{-}+H_3O^{+} & K_1 &= 7.1\cdot 10^{-4} \\ H_2C_6H_5O_7^{-}+H_2O &\rightarrow HC_6H_5O_7^{2-}+H_3O^{+} & K_2 &= 1.7\cdot 10^{-5} \\ HC_6H_5O_7^{2-}+H_2O &\rightarrow C_6H_5O_7^{3-}+H_3O^{+} & K_3 &= 6.4\cdot 10^{-6} \end{aligned} \tag{11.32}$$

(a) If .01 moles of citric acid is added to 1 kg of pure water, what is the pH of the solution?

(b) Now, 1 millimole of HCl is also added to the solution. What is the molality of $H_3C_6H_5O_7$, $H_2C_6H_5O_7^{-}$, $HC_6H_5O_7^{-2}$, and $C_6H_5O_7^{-3}$?

Extension:
Consider the deprotonation of EDTA. The equilibrium constants are,

$$\begin{aligned}
&\mathrm{H_6EDTA^{2+} + H_2O \rightarrow H_5EDTA^{1+} + H_3O^+} && K_1 = 1.0 \\
&\mathrm{H_5EDTA^{+} + H_2O \rightarrow H_4EDTA + H_3O^+} && K_2 = 3.2\cdot 10^{-2} \\
&\mathrm{H_4EDTA + H_2O \rightarrow H_3EDTA^{-} + H_3O^+} && K_3 = 1.0\cdot 10^{-2} \\
&\mathrm{H_3EDTA^{-} + H_2O \rightarrow H_2EDTA^{2-} + H_3O^+} && K_4 = 2.0\cdot 10^{-3} \\
&\mathrm{H_2EDTA^{2-} + H_2O \rightarrow H_1EDTA^{3-} + H_3O^+} && K_5 = 7.4\cdot 10^{-7} \\
&\mathrm{H_1EDTA^{3-} + H_2O \rightarrow EDTA^{4-} + H_3O^+} && K_6 = 4.3\cdot 10^{-11}
\end{aligned} \tag{11.33}$$

(a) If X moles of EDTA is added to 1 kg of solution, plot $[H_3O^+]$ vs. X.
(b) If you titrate EDTA with HCl, give the concentrations of $[H_nEDTA^{n-6}]$ vs. pH. (That is, plot the concentration of EDTA vs. $-\log_{10}[H_3O^+]$.

Extension:
In many proteins, the binding of a signaling molecule induces a conformational change in the protein, for example from a "closed" to a "open" configuration. This can be described by the reactions,

$$\begin{aligned}
&\text{enzyme} + \text{substrate} \rightleftarrows \text{enzyme-substrate} && K_{\text{bind}} \\
&\text{enzyme-substrate(closed)} \rightleftarrows \text{enzyme-substrate(open)} && K_{\text{open}}
\end{aligned} \tag{11.34}$$

Assume that the initial concentration of the enzyme is 1 nanomole/kg of water, and that the initial concentration of substrate is 10 nanomoles/kg of water. Assume that $K_{\text{bind}} = 10$ and $K_{\text{open}} = 10$. Compute the molality of the open enzyme-substrate configuration.

Further thought:
After one has solved one problem, one sometimes needs to solve a different problem with slightly different conditions. For example, if the temperature changes, the equilibrium constants will also change, and that will change the final concentrations. To do this, one needs to determine how the progresses of reactions depend on the temperature, which means that one needs to describe how the solutions to the nonlinear equations depend on the temperature. Often determining this dependence is quite difficult, but there are established methods for doing it, called perturbation theory. The key is to notice that we can write

$$\frac{d\xi}{dT} = \sum_{r\in\text{rxns}} \frac{d\xi}{dK_r}\frac{dK_r}{dT} = \sum_{r\in\text{rxns}} \left(\frac{dK_r}{d\xi}\right)^{-1} \frac{dK_r}{dT} \tag{11.35}$$

Using this approach, write an expression for the pH of a citric acid solution on temperature.

References:
The primary purpose of this module was to introduce Newton's method for nonlinear equations:

https://en.wikipedia.org/wiki/Newton%27s_method
https://www.math.ohiou.edu/courses/math3600/lecture13.pdf
http://www.seas.ucla.edu/~vandenbe/103/lectures/newton.pdf
http://www.iitg.ac.in/kartha/CE601/Solved/Example4.pdf

The specific systems we explored were based on simultaneous chemical equilibria, but similar problems appear in chemical kinetics, industrial processes (e.g., flow reactors), and many other contexts.

http://www.pearsonhighered.com/samplechapter/0130138517.pdf (See example 1.4)
http://ocw.usu.edu/Civil_and_Environmental_Engineering/Numerical_Methods_in_Civil_Engineering/NonLinearEquationsMatlab.pdf
http://pubsonline.informs.org/doi/pdf/10.1287/opre.34.3.345
http://gw-chimie.math.unibuc.ro/anunivch/2005-2/AUBCh2005XIV2395400.pdf
http://pubs.sciepub.com/wjce/2/4/2/

There are great (and comprehensive) notes on a variety of mathematical problems, including these and many more, at:

http://www.math.umn.edu/~olver/