Chemistry 146 Lecture Problems
Calculating the Equlibrium for a Weak Acid

For nitrous acid $K_a = 4.5*10^{-4}$

What is the pH and pOH of a 1.0 M nitrous acid solution?
What is the pH and pOH of a 0.001 M nitrous acid solution?
What is the pH and pOH of a 10^{-8} M nitrous acid solution?

First I will solve the problem making NO assumptions. This is a rather complex solution, and you will not be responsible for it this semester. You should, however, look through it use it to understand the simplifications that are normally used. The exact solution is obtained by simultaneously solving for the following equations:

The acid dissociation constant	$K_a := 4.5 \cdot 10^{-4}$	$K_a = \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}}$
The conservation of mass	$C_{total} := 1.0$	$C_{total} = C_{HNO2} + C_{NO2}$
The autoionization of water	$K_w := 1.0 \cdot 10^{-14}$	$K_w = C_{H3O} \cdot C_{OH}$
Balanced charge	$C_{OH} + C_{NO2} = C_{H3O}$	

The first part of this solution is to make some substitutions and derive an equation with fewer variables. From the information above, we have 4 unknowns and four independent equations. There is an exact solution for this problem.

From the expression for K_w:

$K_w = C_{H3O} \cdot C_{OH}$ Rearranges to give: $C_{OH} = \frac{K_w}{C_{H3O}}$

Then substitute this expression for $[OH^-]$ in the charge balance equation:

$C_{OH} + C_{NO2} = C_{H3O}$ To give: $\frac{K_w}{C_{H3O}} + C_{NO2} = C_{H3O}$

Solve this for $[NO_2^-]$: $C_{NO2} = C_{H3O} - \frac{K_w}{C_{H3O}}$

Then substitute this into the equation for the total mass:

$$C_{total} = C_{HNO2} + C_{NO2}$$ To give: $$C_{total} = C_{HNO2} - \frac{K_w}{C_{H3O}} + C_{H3O}$$

And rearrange to solve for [HNO_2]: $$C_{HNO2} = C_{total} + \frac{K_w}{C_{H3O}} - C_{H3O}$$

Finally substitute these expressions for [HNO_2] and [NO_2^-] into the equation for K_a:

$$K_a = \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}}$$ To give: $$K_a = C_{H3O} \cdot \frac{\left(C_{H3O} - \frac{K_w}{C_{H3O}}\right)}{\left(C_{total} + \frac{K_w}{C_{H3O}} - C_{H3O}\right)}$$

Now substitute in values for known variables:

$$4.5 \cdot 10^{-4} = C_{H3O} \cdot \frac{\left(C_{H3O} - \frac{10^{-14}}{C_{H3O}}\right)}{\left(1.0 + 1.0 \cdot \frac{10^{-14}}{C_{H3O}} - C_{H3O}\right)}$$

Relate this expression to the balanced equation.

And solve the resulting cubic equation:

$$C_{H3O} = \begin{bmatrix} 2.0989396644972356931 \cdot 10^{-2} + 2. \cdot 10^{-22} \cdot i \\ -2.1439396644962356932 \cdot 10^{-2} + 9. \cdot 10^{-22} \cdot i \\ -1.0 \cdot 10^{-14} - 9. \cdot 10^{-22} \cdot i \end{bmatrix}$$

Note the above expression shows three different solutions to the equation. This is just like obtaining two roots from the quadratic equation. Two of the answers are negative numbers, which do not make any physical sense for this problem. The i's shown in the answer are the magnitude of the imaginary vector in the solution (Do you recall that the square root of -1, is an imaginary number?). As you can see the magnitude of the imaginary vector (10^{-22}) is exceedingly small. I am uncertain if it is a result of the mathematical software that I used to solve the cubic or it is a "real" imaginary number. We'll just ignore it and give the answer as

[$H3O^+$] = $2.0989 * 10^{-2}$

Now from the expressions derived above I'll solve using the exact solution for the other initial concentrations of HNO_2:

For 0.001 M acid:

$$4.5\cdot10^{-4}=C_{H3O}\cdot\frac{\left(C_{H3O}-\frac{10^{-14}}{C_{H3O}}\right)}{\left(0.001+1.0\cdot\frac{10^{-14}}{C_{H3O}}-C_{H3O}\right)}$$

$$C_{H3O}=\begin{bmatrix}4.8254859856089432093\cdot10^{-4}\\ -9.3254858856089464316\cdot10^{-4}-1.\cdot10^{-23}\cdot i\\ -9.99999967778\cdot10^{-12}+1.\cdot10^{-23}\cdot i\end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+]$ = 4.825*10^{-4} M

For 10^{-8} M acid:

$$4.5\cdot10^{-4}=C_{H3O}\cdot\frac{\left(C_{H3O}-\frac{10^{-14}}{C_{H3O}}\right)}{\left(10^{-8}+1.0\cdot\frac{10^{-14}}{C_{H3O}}-C_{H3O}\right)}$$

$$C_{H3O}=\begin{bmatrix}1.051236958954673\cdot10^{-7}+1.\cdot10^{-23}\cdot i\\ -4.5000999977828143706\cdot10^{-4}\\ -9.512391761403024\cdot10^{-8}\end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+]$ = 1.051*10^{-7} M

Now lets try the problem again with some simplifying assumptions using just the following three equations and three unknowns:

The acid dissociation constant $K_a := 4.5 \cdot 10^{-4}$ $$K_a = \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}}$$

The conservation of mass $C_{total} := 1.0$ $$C_{total} = C_{HNO2} + C_{NO2}$$

Assumes $[H_3O^+]$ and $[NO_2^-]$ are equal,
ie: no contribution from autoionization of water

$$C_{H3O} = C_{NO2}$$

Then the substituting into the expression for K_a:

$$K_a = \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}} \quad \text{To give:} \quad K_a = \frac{C_{H3O}^2}{C_{HNO2}}$$

and the expression for total concentration rearranges:

$$C_{total} = C_{HNO2} + C_{NO2} \quad \text{To give:} \quad C_{HNO2} = C_{total} - C_{H3O}$$

Which the substitutes into the new expression for Ka:

$$K_a = \frac{C_{H3O}^2}{C_{HNO2}} \quad \text{To give} \quad K_a = \frac{C_{H3O}^2}{\left(C_{total} - C_{H3O}\right)}$$

Now enter the known variables: $$4.5 \cdot 10^{-4} = \frac{C_{H3O}^2}{\left(1.0 - C_{H3O}\right)}$$

And solve for [H3O+]: $$C_{H3O} = \begin{bmatrix} 2.0989396644731614898 \cdot 10^{-2} \\ -2.1439396644731614898 \cdot 10^{-2} \end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+] = 2.0989 \cdot 10^{-2}$ M

Now from the expressions derived above I'll solve for the other initial concentrations of HNO_2 using the same assumptions:

For 0.001 M acid:

$$4.5\cdot 10^{-4} = \frac{C_{H3O}^{2}}{\left(0.001 - C_{H3O}\right)}$$

$$C_{H3O} = \begin{bmatrix} 4.8254858490424528585\cdot 10^{-4} \\ -9.3254858490424528585\cdot 10^{-4} \end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+]$ = 4.825*10^{-4} M

For 10^{-8} M acid:

$$4.5\cdot 10^{-4} = \frac{C_{H3O}^{2}}{\left(10^{-8} - C_{H3O}\right)}$$

$$\begin{bmatrix} 9.99977778765377\cdot 10^{-9} \\ -4.5000999977778765377\cdot 10^{-4} \end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+]$ = 10.0*10^{-9} M

NOTE: there are clearly some significant problems with this approximation. Compare it to the exact solution.

Finally, lets make it even simpler and avoid the quadratic expression.

Starting by assuming that [H3O+] is much smaller than the total concentration. Then the expression derived for Ka above:

$$K_a = \frac{C_{H3O}^2}{\left(C_{total} - C_{H3O}\right)}$$ Simplifies to: $$K_a = \frac{C_{H3O}^2}{C_{total}}$$

Substituting in appropriate values: $$4.5 \cdot 10^{-4} = \frac{C_{H3O}^2}{(1.0)}$$

Then solves as: $$C_{H3O} = \sqrt{4.5 \cdot 10^{-4}}$$

$$C_{H3O} = 2.1213203435596425732 \cdot 10^{-2}$$

For other acid concentrations:

0.001 M acid: $$4.5 \cdot 10^{-4} = \frac{C_{H3O}^2}{(0.001)}$$

$$C_{H3O} = \begin{bmatrix} -6.7082039324993690892 \cdot 10^{-4} \\ 6.7082039324993690892 \cdot 10^{-4} \end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+] = 6.708 * 10^{-4}$ M

10-8 M acid: $$4.5 \cdot 10^{-4} = \frac{C_{H3O}^2}{\left(10^{-8}\right)}$$

$$C_{H3O} = \begin{bmatrix} -2.1213203435596425732 \cdot 10^{-6} \\ 2.1213203435596425732 \cdot 10^{-6} \end{bmatrix}$$

The only physically reasonable root is:

$[H_3O^+] = 2.121 * 10^{-6}$ M

Finally, lets tabulate all the results and see how they compare:

	Exact	No Significant Autoionization	No Significant Dissociation
10^{0} M HNO_2	$2.0989*10^{-2}$	$2.0989*10^{-2}$	$2.121*10^{-2}$
10^{-3} M HNO_2	$4.825*10^{-4}$	$4.825*10^{-4}$	$6.708*10^{-4}$
10^{-8} M HNO_2	$1.051*10^{-7}$	$10.00*10^{-9}$	$2.121*10^{-6}$

Now returning to the original equations, to double check the solutions:

The acid dissociation constant $\quad K_a := 4.5 \cdot 10^{-4} \quad K_a = \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}}$

The conservation of mass $\quad C_{total} := 1.0 \quad C_{total} = C_{HNO2} + C_{NO2}$

The autoionization of water $\quad K_w := 1.0 \cdot 10^{-14} \quad K_w = C_{H3O} \cdot C_{OH}$

Balanced charge $\quad C_{OH} + C_{NO2} = C_{H3O}$

For the 1 M HNO2 solution: $\quad C_{H3O} := 2.0989 \cdot 10^{-2}$

$K_w = C_{H3O} \cdot C_{OH}$ has solution(s) $\quad C_{OH} := \frac{K_w}{C_{H3O}}$

$C_{OH} = 4.764 \cdot 10^{-13}$

$C_{OH} + C_{NO2} = C_{H3O}$ has solution(s) $\quad C_{NO2} := -C_{OH} + C_{H3O}$

$C_{NO2} = 0.021$

$C_{total} = C_{HNO2} + C_{NO2}$ has solution(s) $\quad C_{HNO2} := C_{total} - C_{NO2}$

$C_{HNO2} = 0.979$

Substituting in to the original equation for Ka:

$K_a := \frac{C_{H3O} \cdot C_{NO2}}{C_{HNO2}}$ Yields $\quad K_a = 4.5 \cdot 10^{-4}$

Since this is equivilent to the original expression for Ka, all the equations are consistent.

Now that you have seen this worked out, go back and look through the assumptions. How far off were they in each case? If you want to really understand this, you will need to spend some serious time looking at these problems. To help you I will include some expansions of the equation for the exact solution (To help you see the math).

$$K_a = C_{H3O} \cdot \frac{\left(C_{H3O} - \frac{K_w}{C_{H3O}}\right)}{\left(C_{total} + \frac{K_w}{C_{H3O}} - C_{H3O}\right)}$$

expands to

$$K_a = \frac{C_{H3O}^{2}}{\left(C_{total} + \frac{K_w}{C_{H3O}} - C_{H3O}\right)} - \frac{1}{\left(C_{total} + \frac{K_w}{C_{H3O}} - C_{H3O}\right)} \cdot K_w$$

simplifies to

$$K_a = \frac{C_{H3O}^{3}}{\left(C_{total} \cdot C_{H3O} + K_w - C_{H3O}^{2}\right)} - \frac{C_{H3O}}{\left(C_{total} \cdot C_{H3O} + K_w - C_{H3O}^{2}\right)} \cdot K_w$$

simplifies to

$$K_a \cdot \left(C_{total} \cdot C_{H3O} + K_w - C_{H3O}^{2}\right) - \left(C_{H3O}^{3} - C_{H3O} \cdot K_w\right) = 0$$

simplifies to

$$K_a \cdot C_{total} \cdot C_{H3O} + K_a \cdot K_w - K_a \cdot C_{H3O}^{2} - C_{H3O}^{3} + C_{H3O} \cdot K_w = 0$$

by collecting terms, yields

$$-C_{H3O}^{3} - K_a \cdot C_{H3O}^{2} + \left(K_a \cdot C_{total} + K_w\right) \cdot C_{H3O} + K_a \cdot K_w = 0$$

Multiply by -1:

$$C_{H3O}^{3} + K_a \cdot C_{H3O}^{2} - K_a \cdot C_{total} \cdot C_{H3O} - C_{H3O} \cdot K_w - K_a \cdot K_w = 0$$

Now enter values for known variables:

$$C_{H3O}^{3} + 4.5 \cdot 10^{-4} \cdot C_{H3O}^{2} - 4.5 \cdot 10^{-4} \cdot C_{H3O} - 4.5 \cdot 10^{-18} = 0$$

has solution(s)

$$\begin{bmatrix} 2.0989396644736667928 \cdot 10^{-2} - 1. \cdot 10^{-22} \cdot i \\ -2.1439396644726667928 \cdot 10^{-2} \\ -1.0 \cdot 10^{-14} \end{bmatrix}$$

A graph of this function is shown below, the solution is where the line crosses 0 on the Y axis:

$$i := 1, 2 .. 100$$

$$C_{H3O_i} := \frac{i}{3000} - .01$$

$$Y_i := \left(C_{H3O_i}\right)^3 + 4.5 \cdot 10^{-4} \cdot \left(C_{H3O_i}\right)^2 - 4.5 \cdot 10^{-4} \cdot C_{H3O_i} - 4.5 \cdot 10^{-18}$$