## Chem 116 POGIL Worksheet - Week 10 - Solutions Weak Acid and Base Equilibria

## Key Questions

1. A 0.0100 M solution of a weak acid HA has a pH of 2.60 . What is the value of $K_{a}$ for the acid? [Hint: What is the actual concentration of undissociated HA, [HA], in this solution?]

$$
\mathrm{pH}=2.60 \Rightarrow\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.5 \times 10^{-3} \mathrm{M}
$$

We can assume that the acid is the major source of hydronium ion and that water contributes little to the total $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. This concentration of hydronium ion, then, also represents the amount of the initial HA that is lost through hydrolysis. On this basis we have the following equilibrium concentrations:

|  | HA + | $\mathrm{H}_{2} \mathrm{O}$ | $\rightleftharpoons$ | $\mathrm{H}_{3} \mathrm{O}^{+}$ | + | $\mathrm{A}^{-}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Initial | 0.0100 |  |  | $10^{-7}$ |  | 0 |
| Equilibrium | $\begin{array}{r} 0.0100-0.0025 \\ =0.0075 \end{array}$ |  |  | $2.5 \times 10^{-3}$ |  | $2.5 \times 10^{-3}$ |
|  | $K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$ | $=\frac{(2.5}{7}$ |  | $\frac{\left.10^{-3}\right)^{2}}{0^{-3}}=8.3$ |  |  |

2. What is the pH of $4.0 \times 10^{-2} \mathrm{M}$ benzoic acid $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}=\mathrm{HBz}\right)$, for which $K_{a}=6.46 \times$ $10^{-5}$ ? Is it necessary to solve the quadratic equation in this case?

$$
\mathrm{HBz}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Bz}^{-}
$$

The concentration of the acid and the $K_{a}$ fit our criteria to avoid needing the quadratic equation.

$$
\begin{gathered}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\left(4.0 \times 10^{-2}\right)\left(6.46 \times 10^{-5}\right)}=\sqrt{2.5_{84} \times 10^{-6}}=1.6 \times 10^{-3} \mathrm{M}=\left[\mathrm{Bz}^{-}\right]} \\
\mathrm{pH}=2.79
\end{gathered}
$$

The percent dissociation of the benzoic acid, based on our calculation, is

$$
\% \text { dissociation }=\frac{1.6 \times 10^{-3}}{4.0 \times 10^{-2}} \times 100 \%=4.0 \%
$$

This is acceptable, so the quadratic equation was not necessary.
3. Find the concentrations of all species and pH for a $1.0 \times 10^{-3} \mathrm{M}$ HF solution. $K_{a}=6.7 \times$ $10^{-4}$. You will need to find values for $[\mathrm{HF}],\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, $\left[\mathrm{F}^{-}\right]$, and $\left[\mathrm{OH}^{-}\right]$.

$$
\mathrm{HF}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{F}^{-}
$$

Trying the quick method, we obtain

$$
\begin{gathered}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{C_{\mathrm{HA}} K_{a}}=\sqrt{\left(1.0 \times 10^{-3}\right)\left(6.7 \times 10^{-4}\right)}=8.2 \times 10^{-4} \mathrm{M}=\left[\mathrm{F}^{-}\right]} \\
\% \text { dissociation }=\frac{8.2 \times 10^{-4}}{1.0 \times 10^{-3}} \times 100 \%=82 \%
\end{gathered}
$$

This is not acceptable. Notice that $C_{\mathrm{HA}}=1.0 \times 10^{-3}$ and $K_{a}=6.7 \times 10^{-4}$ are within two powers of 10 of each other, suggesting that HF is appreciably dissociated. We must solve the quadratic. This means that we will assume $[\mathrm{HF}]=C_{\mathrm{HF}}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. Substituting into the $K_{a}$ expression:

$$
\begin{gathered}
K_{a}=6.7 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{1.0 \times 10^{-3}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}=6.7 \times 10^{-7}-6.7 \times 10^{-4}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}+6.7 \times 10^{-4}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]-6.7 \times 10^{-7}=0}
\end{gathered}
$$

Solving the quadratic equation and ignoring the negative root $\left(-1.22 \times 10^{-3}\right)$ gives

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.4_{9} \times 10^{-4} \mathrm{M}=\left[\mathrm{F}^{-}\right] \quad \Rightarrow \mathrm{pH}=3.26} \\
& {[\mathrm{HF}]=C_{\mathrm{HF}}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-3}-5.4_{9} \times 10^{-4}=4.5_{1} \times 10^{-4} \mathrm{M}}
\end{aligned}
$$

To find $\left[\mathrm{OH}^{-}\right]$, use $K_{w}$ :

$$
\left[\mathrm{OH}^{-}\right]=\frac{K_{w}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{1.00 \times 10^{-14}}{5.49 \times 10^{-4}}=1.8_{2} \times 10^{-11} \mathrm{M}
$$

4. What is the pH of a 0.120 M solution of $\mathrm{NH}_{3}(a q)$ ? For ammonia, $K_{b}=1.77 \times 10^{-5}$. Is it necessary to solve the quadratic equation? Justify the approach you took, either way.

The hydrolysis equilibrium and the equilibrium concentrations are as follows:

$$
\begin{aligned}
& \mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \underset{x}{\rightleftharpoons} \mathrm{NH}_{4}^{+}+\underset{x}{\mathrm{OH}^{-}} \\
& 0.120-x
\end{aligned}
$$

The analytical concentration of ammonia is 0.120 M , which is greater than $K_{b}=1.77 \times 10^{-5}$ by much more than two powers of 10 . Therefore, we can probably ignore the loss of $\mathrm{NH}_{3}$ from hydrolysis. Thus, we can write

$$
K_{b}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}=\frac{x^{2}}{0.120-x} \approx \frac{x^{2}}{0.120}=1.77 \times 10^{-5}
$$

and

$$
x=\sqrt{(0.120)\left(1.77 \times 10^{-5}\right)}=1.48 \times 10^{-3} \mathrm{M}=\left[\mathrm{OH}^{-}\right]=\left[\mathrm{NH}_{4}^{+}\right]
$$

From this result, the percent hydrolysis is much less than $5 \%$ :

$$
\% \text { hydrolysis }=\frac{1.48 \times 10^{-3}}{0.120} \times 100 \%=1.23 \%
$$

Therefore, we are justified in ignoring loss of $\mathrm{NH}_{3}$ from hydrolysis and avoiding the quadratic equation.

To obtain pH , we could calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{w} /\left[\mathrm{OH}^{-}\right]$, and then get pH ; or we could calculate pOH from our value of $\left[\mathrm{OH}^{-}\right]$, and get pH from $\mathrm{pH}=14.000-\mathrm{pOH}$. Taking the second approach, we have

$$
\mathrm{pOH}=-\log \left(1.48 \times 10^{-3}\right)=2.830 \quad \Rightarrow \mathrm{pH}=14.000-2.830=11.170
$$

5. Sodium hypochlorite, NaOCl , is the active ingredient in chlorine bleach (e.g., Chlorox ${ }^{\ominus}$ ). For hypochlorous acid, $\mathrm{HOCl}, K_{a}=3.0 \times 10^{-8}$.
a. Write the equation for the base hydrolysis equilibrium of the hypochlorite ion.

$$
\mathrm{OCl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HOCl}+\mathrm{OH}^{-}
$$

b. What is the value of $K_{b}$ for the hypochlorite ion?

$$
K_{b}^{\mathrm{OCl}^{-}}=K_{w} / K_{a}^{\mathrm{HOCl}}=\frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}}=3.3_{3} \times 10^{-7}
$$

c. What is the pH of a 0.10 M solution of sodium hypochlorite?

In solution, the 0.10 M NaOCl will break up into $0.10 \mathrm{M} \mathrm{Na}^{+}$and $0.10 \mathrm{M} \mathrm{OCl}^{-}$. Therefore, the analytical concentration of the base is $C_{\mathrm{OCl}^{-}}=0.10 \mathrm{M}$.

$$
\begin{array}{r}
\mathrm{NaOCl} \rightarrow \mathrm{Na}^{+}+\mathrm{OCl}^{-} \\
\mathrm{OCl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HOCl}+\mathrm{OH}^{-} \\
0.10-x
\end{array}
$$

Because the analytical concentration of the base is so much greater than $K_{b}$, loss of $\mathrm{OCl}^{-}$is negligible, and we can assume $\left[\mathrm{OCl}^{-}\right] \approx C_{\mathrm{OCl}^{-}}=0.10 \mathrm{M}$.
Therefore,

$$
\left[\mathrm{OH}^{-}\right]=\sqrt{C_{\mathrm{OCl}^{-}} K_{b}^{\mathrm{OCl}^{-}}}=\sqrt{(0.10)\left(3.3_{3} \times 10^{-7}\right)}=1.8_{25} \times 10^{-4}
$$

From this, $\mathrm{pOH}=3.74$, and $\mathrm{pH}=14.00-4.24=10.26$.
6. Trimethylamine, $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$, is a weak base $\left(K_{b}=6.4 \times 10^{-5}\right)$ that hydrolyzes by the following equilibrium:

$$
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}+\mathrm{OH}^{-}
$$

a. Write the equation for the acid hydrolysis equilibrium of trimethylammonium ion, $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}$.

$$
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

b. What is the value of $K_{a}$ for the trimethylammonium ion, $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}$?

$$
K_{a}^{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}}=K_{w} / K_{b}^{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}}=1.0 \times 10^{-14} / 6.4 \times 10^{-5}=1.5_{6} \times 10^{-10}
$$

c. What is the pH of a 0.12 M solution of trimethylammonium chloride, $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}\right) \mathrm{Cl}$ ?

$$
\begin{aligned}
\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}\right) \mathrm{Cl} \Rightarrow & \left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}+\mathrm{Cl}^{-} \\
& \left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& 0.12-x
\end{aligned}
$$

With $K_{a}=1.5_{6} \times 10^{-10}$, $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}$is a very weak acid, so we can definitely ignore hydrolysis and assume $\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}\right]=C_{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}}=0.12 \mathrm{M}$.

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{C_{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}} K_{a}^{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}}}=\sqrt{(0.12)\left(1.5_{6} \times 10^{-10}\right.}=4.3 \times 10^{-6} \mathrm{M} } \\
& \mathrm{pH}=5.36
\end{aligned}
$$

7. Explain the following observations:
a. $\quad \mathrm{H}_{2} \mathrm{Se}$ is a stronger acid than $\mathrm{H}_{2} \mathrm{~S}$

Se is larger than S , so the $\mathrm{Se}-\mathrm{H}$ bond is weaker, making $\mathrm{H}_{2} \mathrm{Se}$ a stronger acid.
b. $\mathrm{HNO}_{2}$ is a weak acid, but $\mathrm{HNO}_{3}$ is a strong acid
$\mathrm{HNO}_{2}$ has one terminal oxygen, but $\mathrm{HNO}_{3}$ has two, making it a stronger acid.
c. $\mathrm{H}_{3} \mathrm{PO}_{4}$ is a stronger acid than $\mathrm{H}_{3} \mathrm{AsO}_{4}$

P is more electronegative than As, making $\mathrm{H}_{3} \mathrm{PO}_{4}$ a stronger acid.
d. $\mathrm{FCH}_{2} \mathrm{CO}_{2} \mathrm{H}$ is a stronger acid than $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$

Electronegative fluorine withdraws electron density from the - OH bond of the carboxyl group, $-\mathrm{CO}_{2} \mathrm{H}$, making $\mathrm{FCH}_{2} \mathrm{CO}_{2} \mathrm{H}$ a stronger acid.
8. What is the pH of a solution prepared by adding 0.20 mole of formic acid, $\mathrm{HCO}_{2} \mathrm{H}$, and 0.25 mole of sodium formate, $\mathrm{NaHCO}_{2}$, in enough water to make a liter of solution? The $K_{a}$ of formic acid is $1.8 \times 10^{-4}$.

$$
\begin{aligned}
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{2}^{-}\right]}{\left[\mathrm{HCO}_{2} \mathrm{H}\right]} & =\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right](0.25)}{0.20}=1.8 \times 10^{-4} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =1.44 \times 10^{-4} \\
\mathrm{pH} & =3.84
\end{aligned}
$$

9. What is the pH of a solution prepared by adding 0.60 mole of formic acid and 0.75 mole of sodium formate in enough water to make a liter of solution? How does your answer compare to the answer you obtained in Key Question 8? Explain.

$$
\begin{aligned}
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{2}^{-}\right]}{\left[\mathrm{HCO}_{2} \mathrm{H}\right]} & =\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right](0.75)}{0.60}=1.8 \times 10^{-4} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =1.44 \times 10^{-4} \\
\mathrm{pH} & =3.84
\end{aligned}
$$

The pH is the same in both cases because the ratio $\left[\mathrm{HCO}_{2}^{-}\right] /\left[\mathrm{HCO}_{2} \mathrm{H}\right]$ is the same in both cases.
10. The solution prepared in Key Question 9 was diluted with enough water to make ten liters of solution. What is the pH of the dilute solution? How does it compare to the previous two solutions? Explain.

Diluting to ten liters makes the analytical concentrations of both the acid and its conjugate base become one tenth what they were; i.e.,

$$
C_{\mathrm{HCO}_{2} \mathrm{H}}=0.060 \mathrm{M} \quad . \quad C_{\mathrm{HCO}_{2}^{-}}=0.075 \mathrm{M}
$$

But the ratio $\left[\mathrm{HCO}_{2}^{-}\right] /\left[\mathrm{HCO}_{2} \mathrm{H}\right]$ remains the same as it was in the solutions in Key Questions 8 and 9, so the pH is still 3.84.

$$
\begin{aligned}
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{2}^{-}\right]}{\left[\mathrm{HCO}_{2} \mathrm{H}\right]} & =\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right](0.075)}{0.060}=1.8 \times 10^{-4} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =1.44 \times 10^{-4} \\
\mathrm{pH} & =3.84
\end{aligned}
$$

It is the ratio between the concentrations of the conjugate pair that fixes the pH in solutions of this type, not the actual concentrations themselves.
11. A student wishes to prepare a buffer with a pH of 4.52 . She starts by preparing one liter of 0.10 M formic acid, $\mathrm{HCO}_{2} \mathrm{H}$. How many grams of sodium formate, $\mathrm{NaHCO}_{2}$, must she add to the solution to achieve the desired pH ? $K_{a}=1.8 \times 10^{-4}$ for formic acid. The formula weight of sodium formate is 68.00 u .

First we need to determine what concentration of hydronium ion corresponds to $\mathrm{pH}=4.54$.

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-4.52}=3.0 \times 10^{-5} \mathrm{M}
$$

Next, by substituting into the $K_{a}$ expression, we determine the ratio $\left[\mathrm{HCO}_{2}^{-}\right] /\left[\mathrm{HCO}_{2} \mathrm{H}\right]$ that will give $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.0 \times 10^{-5} \mathrm{M}$..

$$
\frac{K_{a}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{\left[\mathrm{HCO}_{2}^{-}\right]}{\left[\mathrm{HCO}_{2} \mathrm{H}\right]}=\frac{1.8 \times 10^{-4}}{3.0 \times 10^{-5}}=6.0
$$

One liter of $0.10 \mathrm{M} \mathrm{HCO}_{2} \mathrm{H}$ contains 0.10 mol of the acid. Therefore,

$$
\mathrm{g} \mathrm{NaHCO}_{2}=\left(0.10 \mathrm{~mol} \mathrm{HCO}_{2} \mathrm{H}\right)\left(\frac{6 \mathrm{~mol} \mathrm{NaHCO}}{2}\right)\left(\frac{68.00 \mathrm{~g} \mathrm{NaHCO}_{2}}{1 \mathrm{~mol} \mathrm{HCO}}{ }_{2} \mathrm{H}\right)\left(\frac{\mathrm{mol} \mathrm{NaHCO}}{2} \text { }\right)=40.8 \mathrm{~g} \mathrm{NaHCO}_{2}
$$

12. A buffer solution is made by adding an equal number of moles of the base pyradine, $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$, and the chloride salt of it conjugate base, $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NHCl}$. What is the pH of the buffer solution? The $K_{b}$ of $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ is $1.7 \times 10^{-9}$.

If $\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}\right]=\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}\right]$, then substituting into the $K_{b}$ expression gives

$$
K_{b}=\frac{\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}\right]}=\left[\mathrm{OH}^{-}\right]
$$

For any equimolar mixture of a base and its conjugate acid, $\left[\mathrm{OH}^{-}\right]=K_{b}$, from which it follows $\mathrm{pOH}=\mathrm{p} K_{b}$.

$$
\begin{aligned}
& \mathrm{pOH}=-\log \left(1.7 \times 10^{-9}\right)=8.77 \\
& \mathrm{pH}=14.00-\mathrm{pH}=5.23
\end{aligned}
$$

