## Systematic Approach to pH, Equilibrium, and Titrimetry

Use any tools you wish to perform these calculations. Some of these problems can best be solved by using mathematical or technological aids (successive approximations, quadratic formula, calculator solver, etc.). Computer use is recommended wherever appropriate and possible.

## pH Calculations of Simple Systems

1. What is the pH of 0.15 M HCl ?

HCl is a strong acid, so $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.15 \mathrm{M}$

$$
\mathrm{pH}=-\log (0.15)=0.82
$$

2. What is the pH of 0.15 M NaOH ?

NaOH is a strong base, so $\left[\mathrm{OH}^{-}\right]=0.15 \mathrm{M}$

$$
\mathrm{pH}=14-\mathrm{pOH}=14-0.82
$$

$\mathrm{pH}=13.2$
3. Calculate the pH of 0.010 M formic acid.

$$
\mathrm{HCO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O} \underset{\mathrm{HCO}_{2}^{-}}{\rightleftarrows}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-4}
$$

Without derivation:

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{2}^{-}\right]}{\left[\mathrm{HCO}_{2} \mathrm{H}\right]} \\
& K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{\mathrm{C}_{\mathrm{HCO}_{2} \mathrm{H}}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \approx \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{\mathrm{C}_{\mathrm{HCO}_{2} \mathrm{H}}}
\end{aligned}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{0.010\left(1.8 \times 10^{-4}\right)}=1.3 \times 10^{-3} \mathrm{M}
$$

Check assumption:

$$
\frac{1.3 \times 10^{-3}}{0.010} \times 100=13 \%
$$

Assumption fails, must solve rigorously:

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.25 \times 10^{-3} \mathrm{M}} \\
& \mathrm{pH}=2.90
\end{aligned}
$$

Not assigned, but percentage acid which is ionized is calculated
$\%$ ionized $=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\mathrm{C}_{\mathrm{HCO}_{2} \mathrm{H}}} \times 100 \%=\frac{1.25 \times 10^{-3}}{0.010} \times 100 \%=12.5 \%$ ionized
4. Calculate the pH of 0.00010 M formic acid
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{\mathrm{C}_{\mathrm{HCO}_{2} \mathrm{H}}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}$
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{1.0 \times 10^{-4}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=7.2 \times 10^{-5} \mathrm{M}$
$\mathrm{pH}=4.15$
$\%$ ionized $=\frac{7.2 \times 10^{-5}}{1.0 \times 10^{-4}} \times 100 \%=72 \%$
It is interesting to note that as the acid becomes more dilute, it ionizes more. This is true for all weak electrolytes.
5. Generate the titration curve for the titration of 20 mL of 0.1 M NaOH with $0.2 \mathrm{M} \mathrm{HNO}_{3}$. Use only as many points as you think is necessary.

6. Generate the titration curve for the titration of 20 mL of 0.1 M HCl with 0.2 M KOH .
7. What is the pH of 0.10 M sodium pyruvate?

For pyruvic acid (HOpyr), $\mathrm{K}_{\mathrm{a}}=3.2 \times 10^{-3}$ so $\mathrm{K}_{\mathrm{b}}=3.13 \times 10^{-12}$
Opyr ${ }^{-}+\mathrm{H}_{2} \mathrm{O} \underset{\mathrm{HOpyr}+\mathrm{OH}^{-}}{\rightleftarrows}$

$$
K_{b}=\frac{\left[\mathrm{OH}^{-}\right][\mathrm{HOpyr}]}{\left[\mathrm{Opyr}^{-}\right]}=\frac{\left[\mathrm{OH}^{-}\right]^{2}}{\mathrm{C}_{\mathrm{Opyr}^{-}}-\left[\mathrm{OH}^{-}\right]} \approx \frac{\left[\mathrm{OH}^{-}\right]^{2}}{\mathrm{C}_{\mathrm{Opyr}^{-}}}
$$

$$
\left[\mathrm{OH}^{-}\right]=\sqrt{(0.10)\left(3.2 \times 10^{-3}\right)}=5.59 \times 10^{-7} \mathrm{M} \mathrm{OH}^{-}
$$

$$
\mathrm{pOH}=6.25
$$

$$
\mathrm{pH}=7.75
$$

8. Approximate the pH of $10^{-5} \mathrm{M}$ pyruvic acid.

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{\mathrm{C}_{\mathrm{Opyr}}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}
$$

No Assumptions allowed except that $\left[\mathrm{OH}^{-}\right]$is small

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}{1.0 \times 10^{-5}-\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=9.97 \times 10^{-6} \mathrm{M}} \\
& \mathrm{pH}=5.00
\end{aligned}
$$

For all practical purposes, the pyruvic acid is completely ionized

