| Name | Formula | K | pK, |
| :---: | :---: | :---: | :---: |
| Hydroiodic acid | HI | large $\sim 10^{11}$ | -11 |
| Perchloric acid | $\mathrm{HClO}_{4}$ | large $\sim 10^{10}$ | -10 |
| Hydrobromic acid | HBr | large $\sim 10^{9}$ | -9 |
| Hydrochloric acid | HCl | large $\sim 10^{\prime}$ | -7 |
| Chloric acid | $\mathrm{HClO}_{3}$ | large $\sim 10^{3}$ | -3 |
| Sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | large $\sim 10^{2}$ | -2 |
| Nitric acid | $\mathrm{HNO}_{3}$ | large ~10 | -1 |
| Hydronium ion | $\mathrm{H}_{3} \mathrm{O}^{+}$ | 1.0 | 0 |
| Trichloroacetic acid | $\mathrm{CCl}_{3} \mathrm{CO}_{2} \mathrm{H}$ | $3.0 \times 10^{-1}$ | 0.52 |
| Iodic acid | $\mathrm{HIO}_{3}$ | $1.6 \times 10^{-1}$ | 0.80 |
| Sulfurous acid | $\mathrm{H}_{2} \mathrm{SO}_{3}$ | $1.5 \times 10^{-2}$ | 1.82 |
| Hydrogen sulfate | $\mathrm{HSO}_{4}^{-}$ | $1.2 \times 10^{-2}$ | 1.92 |
| Chlorous acid | $\mathrm{HClO}_{2}$ | $1.1 \times 10^{-2}$ | 1.96 |
| Phosphoric acid | $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $7.5 \times 10^{-3}$ | 2.12 |
| Hydrofluoric acid | HF | $6.8 \times 10^{-4}$ | 3.17 |
| Nitrous acid | $\mathrm{HNO}_{2}$ | $4.5 \times 10^{-4}$ | 3.35 |
| Formic acid | $\mathrm{HCO}_{2} \mathrm{H}$ | $1.8 \times 10^{-4}$ | 3.74 |
| Benzoic acid | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}$ | $6.3 \times 10^{-5}$ | 4.20 |
| Acetic acid | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ | $1.8 \times 10^{-5}$ | 4.74 |
| Propionic acid | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ | $1.3 \times 10^{-5}$ | 4.89 |
| Carbonic acid | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $4.3 \times 10^{-7}$ | 6.37 |
| Hydrogen sulfite | $\mathrm{HSO}_{3}^{-}$ | $1.2 \times 10^{-7}$ | 6.91 |
| Dihydrogen phosphate | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$ | $6.2 \times 10^{-8}$ | 7.21 |
| Hypochlorous acid | HClO | $3.0 \times 10^{-8}$ | 7.52 |
| Hypobromous acid | HBrO | $2.3 \times 10^{-9}$ | 8.64 |
| Ammonium ion | $\mathrm{NH}_{4}^{+}$ | $5.6 \times 10^{-10}$ | 9.26 |
| Hydrocyanic acid | HCN | $4.0 \times 10^{-10}$ | 9.40 |
| Phenol | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}$ | $1.6 \times 10^{-10}$ | 9.80 |
| Hydrogen carbonate | $\mathrm{HCO}_{3}^{-}$ | $5.6 \times 10^{-11}$ | 10.25 |
| Hypoiodous acid | HIO | $2.3 \times 10^{-11}$ | 10.64 |
| Hydrogen phosphate | $\mathrm{HPO}_{4}^{2-}$ | $3.6 \times 10^{-13}$ | 12.44 |


| Metal Ion | $\mathrm{K}_{\mathrm{a}}$ | $\mathrm{pK}_{\mathbf{a}}$ |
| :--- | :--- | :--- |
| $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | $3.5 \times 10^{-3}$ | 2.46 |
| $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | $1.3 \times 10^{-4}$ | 3.89 |
| $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | $7.9 \times 10^{-6}$ | 5.10 |
| $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ | $3.2 \times 10^{-8}$ | 7.49 |
| $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ | $1.3 \times 10^{-9}$ | 8.89 |
| $\left[{\left.\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}}^{2+5}\right.$ | $2.5 \times 10^{-11}$ | 10.6 |
| $\left[\mathrm{Mg}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ | zero |  |
| $\left[\mathrm{Na}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{+}$ | zero |  |

## Fun with Acid/base equilibrium

- Today we have two goals:
$>$ Calculating the pH of complex salt solutions
> Polyprotic acids
- The big picture:
$>$ All these aqueous acid/base problems are examples of simultaneous equilibrium.
$>$ This general situation is very common in chemical engineering.
- Batch fed reactions and fermentations
- We'll be looking at some acid/base examples, but all the concepts are the same.


## Fun with Acid/base equilibrium

- In the first example we have to worry about the anion:

$$
\mathrm{NaCN}(\mathrm{~s}) \rightleftharpoons \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{CN}^{-}(\mathrm{aq})
$$

$\mathrm{Na}^{+}$: Group 1A metal, just solvates
CN : Anion of a weak acid. Will equilibrate in water.
$\mathrm{HCN} \mathrm{K}_{\mathrm{a}}=4 \times 10^{-10}$

It is imperative to understand the species you have in solution. It's why we memorized all those ions and the strong acids!

## Fun with Acid/base equilibrium

- Example: What is the pH of a 1 M solution of NaCN ?

$$
\mathrm{CN}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \stackrel{\mathrm{~K}_{\mathrm{b}}}{=} \mathrm{HCN}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

Equil: $1-x$
x
x

## Fun with Acid/base equilibrium

## $\mathrm{CN}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \stackrel{\mathrm{K}_{\mathrm{b}}}{\rightleftharpoons} \mathrm{HCN}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$ <br> Equil: 1 - x <br> X X

$$
K_{b}=\frac{(x)(x)}{1.0-(x)}
$$

$$
K_{w}=K_{a} K_{b}
$$

$$
K_{b}=\frac{K_{w}}{K_{a}}=\frac{1 \times 10^{-14}}{4 \times 10^{-10}}=2.5 \times 10^{-5}
$$

$2.5 \times 10^{-5}=\frac{(x)(x)}{1.0-(x)}=x^{2}(\mathrm{x}$ has to be much smaller than 1.0$)$
$5 \times 10^{-3}=x$
$\left[\mathrm{OH}^{-}\right]=5 \times 10^{-3}$
pOH $=-\log \left(5 \times 10^{-3}\right)=2.3$
$p H=14-p O H=14-2.3=11.7$

## Fun with Acid/base equilibrium

- Now we'll look at a more complicated situation: when both the anion and the cation are the salts of a weak acid/base.
- Example what is the pH of a 0.2 M solution of $\mathrm{NH}_{4} \mathrm{~F}$ ? $\mathrm{NH}_{4}{ }^{+}$is a weak acid, $\mathrm{F}^{-}$is the conjugate base of a weak acid.
- $\mathrm{NH}_{4} \mathrm{~F}(\mathrm{aq})$
- Salt

$$
=\mathrm{NH}_{4}^{+}(\mathrm{aq}) \quad+
$$

$F^{-}(a q)$
weak base

## Fun with Acid/base equilibrium

Example: What is the pH of a 0.2 M solution of $\mathrm{NH}_{4} \mathrm{~F}$ ? $\mathrm{NH}_{4}{ }^{+}$is a weak acid, $\mathrm{F}^{-}$is the conjugate base of a weak acid (which is a weak base).

$$
\mathrm{NH}_{4} \mathrm{~F} \rightleftharpoons \mathrm{NH}_{4}(\mathrm{aq})+\mathrm{F}^{-}(\mathrm{aq})
$$

$$
\begin{array}{rll}
\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} & \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) & \mathrm{K}_{\mathrm{a}}=5.6 \times 10^{-10} \\
\mathrm{~F}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HF}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) & \mathrm{K}_{\mathrm{b}}=1.47 \times 10^{-11}
\end{array}
$$

## Fun with Acid/base equilibrium

Example: What is the pH of a 0.2 M solution of $\mathrm{NH}_{4} \mathrm{~F}$ ? $\mathrm{NH}_{4}{ }^{+}$is a weak acid, $\mathrm{F}^{-}$is the conjugate base of a weak acid.

$$
\begin{aligned}
& \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{a}}=5.6 \times 10^{-10} \\
& \mathrm{~F}-(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HF}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{b}}=1.47 \times 10^{-11} \\
& \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH} \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O} \quad 1 / \mathrm{K}_{\mathrm{w}}=1 \times 10^{-14}
\end{aligned}
$$

Net: $\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{F}^{-} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{HF}$

$$
K=\frac{K_{a}^{\left(N H^{+}\right)} K_{b}^{F^{-}}}{K_{w}}
$$

## Fun with Acid/base equilibrium

Example: What is the pH of a 0.2 M solution of $\mathrm{NH}_{4} \mathrm{~F}$ ? $\mathrm{NH}_{4}{ }^{+}$is a weak acid, $\mathrm{F}^{-}$is the conjugate base of a weak acid.

$$
\begin{aligned}
& \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{a}}=5.6 \times 10^{-10} \\
& \mathrm{~F}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HF}(\mathrm{aq})+\mathrm{OH}^{(\mathrm{Oq})} \quad \mathrm{K}_{\mathrm{b}}=1.47 \times 10^{-11} \\
& \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O} \\
& 1 / \mathrm{K}_{\mathrm{w}}=1 \times 10^{-14}
\end{aligned}
$$

Net: $\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{F}^{-} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{HF}$

$$
K=\frac{K_{a}^{\left(N H_{4}^{+}\right)} K_{b}^{F^{-}}}{K_{w}}
$$

$$
\begin{aligned}
K & =\frac{\left[N H_{3}\right][\mathrm{HF}]}{\left[N H_{4}^{+}\right]\left[F^{-}\right]} \text {at equilibrium: }\left[N H_{3}\right]=[H F]\left[N H_{4}^{+}\right]\left[F^{-}\right] \\
K=\frac{\left[N H_{3}\right]^{2}}{\left[N H_{4}^{+}\right]^{2}} & K_{a}^{\left(N H_{4}^{+}\right)}=\frac{\left[N H_{3}\right]\left[H_{3} O^{+}\right]}{\left[N H_{4}^{+}\right]} \\
K=\left(\frac{K_{a}^{\left(N H_{4}^{+}\right)}}{\left[H_{3} O^{+}\right]}\right)^{2}=\frac{K_{a}^{\left(N H_{4}^{+}\right)} K_{b}^{F^{-}}}{K_{w}} & \left(\frac{K_{a}^{\left(N H_{4}^{+}\right)}}{\left[H_{3} O^{+}\right]}\right)^{2}=\frac{\left[N H_{3}\right]^{2}}{\left[N H_{4}^{+}\right]^{2}}
\end{aligned}
$$

$$
\begin{aligned}
& K=\frac{\left[N H_{3}\right][H F]}{\left[N H_{4}^{+}\right]\left[F^{-}\right]} \text {at equilibrium: }\left[N H_{3}\right]=[H F] \quad\left[N H_{4}^{+}\right]=\left[F^{-}\right] \\
& K=\frac{\left[N H_{3}\right]^{2}}{\left[N H_{4}^{+}\right]^{2}} \quad K_{a}^{\left(N H_{4}^{+}\right)}=\frac{\left[N H_{3}\right]\left[H_{3} O^{+}\right]}{\left[N H_{4}^{+}\right]} \\
& K=\left(\frac{K_{a}^{\left(N H_{4}^{+}\right)}}{\left[H_{3} O^{+}\right]}\right)^{2}=\frac{K_{a}^{\left(N H_{4}^{+}\right)} K_{b}^{F^{-}}}{K_{w}} \quad\left(\frac{K_{a}^{\left(N H^{+}\right)}}{\left[H_{3} O^{+}\right]}\right)^{2}=\frac{\left[N H_{3}\right]^{2}}{\left[N H_{4}^{+}\right]^{2}} \quad \text { Re } \text { arrange : } \\
& \left(\frac{\left(K_{a}^{\left(N H_{4}^{+}\right)}\right)^{2} K_{w}}{\left.K_{a}^{\left(N H_{4}^{+)} K_{b}^{F^{-}}\right.}\right)=\left(\frac{\left(K_{a}^{\left(N H_{4}^{+}\right)}\right) K_{w}}{K_{b}^{F^{-}}}\right)=\left[H_{3} O^{+}\right]^{2}: \text { Remember: } K_{b}^{F^{-}}=\frac{K_{w}}{K_{a}^{H F}}}\right. \\
& {\left[H_{3} O^{+}\right]^{2}=K_{a}^{\left(N H_{4}^{+}\right)} K_{a}^{H F}} \\
& -\log \left[H_{3} O^{+}\right]^{2}=-\log K_{a}^{\left(N H_{4}^{+}\right)}-\log K_{a}^{H F} \\
& -2 \log \left[H_{3} O^{+}\right]=-\log K_{a}^{\left(N H_{4}^{+}\right)}-\log K_{a}^{H F} \\
& p H=\frac{1}{2}\left\{p K_{a}^{\left(N H_{4}^{+}\right)}+p K_{a}^{H F}\right\} \\
& N H_{4}^{+}: K_{a}=5.6 x 10^{-10} \mathrm{pK}{ }_{a}=-\log \left(5.6 \times 10^{-10}\right)=9.25 \quad F^{-}: K_{a}^{H F}=6.8 \times 10^{-4} p K_{a}=-\log 6.8 \times 10^{-4}=3.17 \\
& p H=\frac{1}{2}\{9.25+3.17\}=6.21 \quad \operatorname{Slightly} \text { acidic! }
\end{aligned}
$$

In general, when both ions have $\mathrm{K}^{\prime}$; $\mathrm{K}_{a}$ and $\mathrm{K}_{b}$ that are $1>\mathrm{K}_{a}$ and $\mathrm{K}_{b}>K_{w}$
$p H=\frac{1}{2}\left\{p K_{a}^{\text {acid }}+p K_{a}^{\text {conj.acid }}\right\}$

# Fun with Acid/base equilibrium: Polyprotic acids 

Now we're gonna get into acids that can give up more than one proton.

Do you think that both H's will dissociate as easily, or do you think they'll be different?

Why?

# Fun with Acid/base equilibrium: Polyprotic acids 

The strongest polyprotic acid is sulfuric acid:

$$
\begin{array}{ll}
\mathrm{H}_{2} \mathrm{SO}_{4} & \rightleftharpoons \mathrm{HSO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a} 1}>1 \\
\mathrm{HSO}_{4}^{-} & \rightleftharpoons \mathrm{SO}_{4}^{2-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a} 1}>1.2 \times 10^{-2}
\end{array}
$$

The pH of sulfuric acid solution will depend on both equilibria. The math is simpler because the first dissociation is complete.

# Fun with Acid/base equilibrium: Polyprotic acids 

Another example, phosphoric acid $\left(\mathrm{H}_{3} \mathrm{PO}_{4}\right)$ :

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} & \mathrm{K}_{\mathrm{a} 1}=7.5 \times 10^{-3} \\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightleftharpoons & \mathrm{HPO}_{4}^{2-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
\mathrm{KPO}_{42}{ }^{2-} \rightleftharpoons 6.2 \times 10^{-8} \\
\mathrm{PO}_{4}^{3-}+\mathrm{H}_{3} \mathrm{O}^{+} & \mathrm{K}_{\mathrm{a} 3}=3.6 \times 10^{-11}
\end{array}
$$

The $10^{5}$ reduction in $\mathrm{K}_{\mathrm{a} 2}$ versus $\mathrm{K}_{\mathrm{a} 1}$ means that the second dissociation will have a negligible effect on the pH of the solution.

Unfortunately, for you, the pH of sulfuric acid depends on both dissociations, so let's do that problem!

## Fun with Acid/base equilibrium: Polyprotic acids

Example, what is the pH of a 0.1 M solution of $\mathrm{H}_{2} \mathrm{SO}_{4}$ ?

|  | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $\mathrm{HSO}_{4}{ }^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{K}_{\mathrm{a} 1}$ big |  |
| :--- | :---: | :---: | :--- | :--- |
| start: | 0.1 M | 0 | 0 |  |
| end: | 0 | 0.1 | 0.1 |  |
|  |  |  |  |  |
|  | $\mathrm{HSO}_{4}{ }^{2-}$ | $\mathrm{SO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{K}_{\mathrm{a} 1}=1.2 \times 10^{-2}$ |  |
| start: | 0.1 | 0 | 0.1 |  |
| end | $0.1-\mathrm{x}$ | x | $0.1+\mathrm{x}$ |  |

## Diprotic acids

## Example, what is the pH of a 0.1 M solution of $\mathrm{H}_{2} \mathrm{SO}_{4}$ ?

|  | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $\mathrm{HSO}_{4}{ }^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{K}_{\mathrm{a} 1}$ big |  |
| :--- | :---: | :---: | :--- | :--- |
| start: | 0.1 M | 0 | 0 |  |
| end: | 0 | 0.1 | 0.1 |  |
|  |  |  |  |  |
|  | $\mathrm{HSO}_{4}{ }^{2-}$ | $\mathrm{SO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{K}_{\mathrm{a} 1}=1.2 \times 10^{-2}$ |  |
| start: | 0.1 | 0 | 0.1 |  |
| end | $0.1-\mathrm{x}$ | x | $0.1+\mathrm{x}$ |  |

$1.2 \times 10^{-2}=\frac{\left[\mathrm{SO}_{4}^{2-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{HSO}_{4}^{-}\right]}=\frac{(x)(.1+x)}{.1-x}$
$1.2 \times 10^{-2}(1-x)=.1 x+x^{2}$
$0=x^{2}+0.112 x-0.0012$
Use the quadratic equation:
$\mathrm{x}=\frac{-0.112 \pm \sqrt{(.112)^{2}-4(1)(-0.0012)}}{2}=0.01$ So at equilibrium:
$\left[\mathrm{SO}_{4}^{2-}\right]=0.01 \mathrm{M}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.1+x=0.11 \mathrm{M}$
$\left[\mathrm{HSO}_{4}^{-}\right]=0.1-x=0.09 \mathrm{M}$
$p H=-\log (0.11)=0.96$
Percent fully ionized: $=\frac{\left[\mathrm{SO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]} \times 100 \%=\frac{0.01 \mathrm{M}}{0.10 \mathrm{M}} \times 100 \%=10 \%$

## More polyprotic acids

- Today we have two goals:
> More polyprotic acids: phosphoric acid and its salts
> Neutralization reactions
- The big picture:
$>$ Why Phosphate? Phosphate is one of the most important buffer systems inside cells.
- We'll be looking at some acid/base examples


## More polyprotic acids

Last Time we talked about a strong polyprotic acid, sulfuric acid. In this case the $\mathrm{K}_{\mathrm{a}}$ 's are close to each other (>1 and $10^{-2}$ ).

However, for weak polyprotic acids, like phosphoric acid or carbonic acid, this is not the case. The $\mathrm{K}_{\mathrm{a}}$ 's are quite far from each other.

We're gonna use phophoric acid as our example:

## Phosphoric acid equilibrium

 phosphoric acid $\left(\mathrm{H}_{3} \mathrm{PO}_{4}\right)$ :$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} & \begin{array}{l}
\mathrm{K}_{\mathrm{a} 1}=7.5 \times 10^{-3} \\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-}
\end{array} \mathrm{HPO}_{4}^{2-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
\mathrm{K}_{\mathrm{a} 2}=6.2 \times 10^{-8} \\
\mathrm{HPO}_{4}^{2-} & \mathrm{PO}_{4}^{3-}+\mathrm{H}_{3} \mathrm{O}^{+}
\end{array} \mathrm{K}_{\mathrm{a} 3}=3.6 \times 10^{-11}
$$

The $10^{5}$ reduction in $\mathrm{K}_{\mathrm{a} 2}$ versus $\mathrm{K}_{\mathrm{a} 1}$ means that the second dissociation will have a negligible effect on the pH of the solution.

## Phosphoric acid equilibrium

Example: What is the pH of $0.1 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$ ? $\mathrm{H}_{3} \mathrm{PO}_{4} \rightleftharpoons \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a} 1}=7.5 \times 10^{-3}$
0.1
0.1-x
0
0
$\mathrm{x} \quad \mathrm{x}$
$K_{a 1}=7.5 \times 10^{-3}=\frac{\left[H_{2} \mathrm{PO}_{4}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{3} P O_{4}\right]}=\frac{(x)(x)}{.1-x}$
$7.5 \times 10^{-4}=x^{2}$
$0.027 M=x$
Oops! This number is too close to .1 to ignore it in denominator:

$$
\begin{aligned}
& \frac{(0.027)^{2}}{.1-0.027} \cong 10 \times 10^{-4} \text { So let's just guess some numbers. Must be smaller: } \\
& \frac{(0.023)^{2}}{.1-0.023} \cong 6.9 \times 10^{-4} \\
& \frac{(0.024)^{2}}{.1-0.024} \cong 7.6 \times 10^{-4} \\
& p H=-\log (0.024)=1.62
\end{aligned}
$$

## Phosphoric acid equilibrium

What is the pH of $0.1 \mathrm{M} \mathrm{NaH}_{2} \mathrm{PO}_{4}$ ?

$$
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightleftharpoons \mathrm{HPO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a} 2}=6.2 \times 10^{-8}
$$

$$
\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O}=\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{OH}^{-} \quad \mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a} 1}=1 \times 10^{-14} / 7.5 \times 10^{-3}=1.3 \times 10^{-12}
$$

It's exactly like $\mathrm{NH}_{4} \mathrm{~F}(\mathrm{~s})$. We have three equilibria, the two above plus water.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightleftharpoons \mathrm{HPO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a} 2}=6.2 \times 10^{-8} \\
& \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \Longrightarrow \mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{OH} \quad \mathrm{~K}_{\mathrm{b} 1}=1.3 \times 10^{-12} \\
& \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O} \quad \mathrm{~K}_{\mathrm{w}}=1 \times 10^{-14} \\
& 2 \mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-} \rightleftharpoons \mathrm{HPO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{PO}_{4} \quad K=\frac{\left(K_{a 2}\right)\left(K_{b 1}\right)}{K_{w}} \\
& p H=\frac{1}{2}\left(p K_{a}^{\left(H_{2} P O_{4}^{-}\right)}+p K_{a}^{\left(H_{3} P_{4}\right)}\right)=\frac{1}{2}\left\{\left(-\log \left(6.2 \times 10^{-8}\right)+-\log \left(7.5 \times 10^{-3}\right)\right\}=4.66\right.
\end{aligned}
$$

## Phosphoric acid equilibrium

So, in general, for an intermediate salt of a polyprotic acid:
$\mathrm{HA}^{-}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{2-} \quad \mathrm{K}_{\mathrm{a} 2}$
$\mathrm{HA}^{-}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}=\mathrm{H}_{2} \mathrm{~A}+\mathrm{OH}^{-} \quad \mathrm{K}_{\mathrm{b} 1}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a} 1}$
$\mathrm{pH}=1 / 2\left\{\mathrm{pKa}_{2}+\mathrm{pKa}_{1}\right\} \quad \mathrm{pH}$ is independent of concentration
pH is average of pKa 's for the
anion and its conjugate acid.
Generally:

$$
\mathrm{MX}(\mathrm{~s}) \rightleftharpoons \underset{1>\mathrm{K}_{\mathrm{a}}>10^{-14}}{\mathrm{M}^{+}(\mathrm{aq})}+\underset{1>\mathrm{K}_{\mathrm{b}}>10^{-14}}{\mathrm{X}^{-}(\mathrm{aq})}
$$

then: $\quad \mathrm{pH}=1 / 2\left\{\mathrm{pKa}_{2}+\mathrm{pKa}_{1}\right\}$

## To summarize for phosphoric acid $\mathrm{H}_{3} \mathrm{PO}_{4}$

1. $\mathrm{H}_{3} \mathrm{PO}_{4}: \mathrm{H}_{3} \mathrm{O}^{+}$will come from $\mathrm{K}_{\mathrm{a} 1}$, the first ionization reaction
2. $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$: amphiprotic; $\mathrm{pH}=1 / 2\left\{\mathrm{pK}_{\mathrm{a} 1}+\mathrm{pK}_{\mathrm{a} 2}\right\}$
3. $\mathrm{HPO}_{4}{ }^{2-}$ : amphiprotic, $\mathrm{pH}=1 / 2\left\{\mathrm{pK}_{\mathrm{a} 2}+\mathrm{pK}_{\mathrm{a} 3}\right\}$
4. $\mathrm{PO}_{4}{ }^{3-}$ : by hydrolysis of water; $\mathrm{k}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a} 3}=2.8 \times 10^{-4}$

## Neutralization -

Acids and bases react in a process called neutralization.

1. Add a strong acid to a weak base, $\mathrm{NH}_{3}$

Acid: $\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}} \gg 1$
Base: $\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \Longrightarrow \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{b}}=1.8 \times 10^{-5}$

$$
\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \mathrm{K}=1 / \mathrm{K}_{\mathrm{w}}
$$

Net: $\quad \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})=\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \mathrm{K}=\mathrm{K}_{\mathrm{b}},\left(1 / \mathrm{K}_{\mathrm{w}}\right)$
2. Weak acid + weak base, example:

## $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{NH}_{3}$

$\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \xlongequal{\Longrightarrow} \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}$
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{K}_{\mathrm{b}}=1.8 \times 10^{-5}$
$\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \mathrm{K}=1 / \mathrm{K}_{\mathrm{w}}$
Net: $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{NH}_{3}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{NH}_{4}{ }^{+} \quad K_{a} K_{b}\left(\frac{1}{K_{w}}\right)=\left(\frac{\left(1.8 \times 10^{-5}\right)\left(1.8 \times 10^{-5}\right)}{1 \times 10^{-14}}\right)=3.2 \times 10^{4}$

## Neutralization -

For any neutralization reaction:

1. strong acid - weak base $K=K_{b} / K_{w}$
2. Strong base - weak acid $K=K_{a} / K_{w}$
3. Weak acid - weak base $K=K_{a} K_{b} / K_{w}$

All that are $>1$ go to completion.

Neutralization reactions are used in titration to evaluate the concentrations and strengths of acids and bases.

## Neutralization -

Example problem:
Problem: 20 mL of 1.0 M HCl are added to 1 L of 0.1 M $\mathrm{NH}_{3}(\mathrm{aq})$ in water. What are the concentrations of $\left[\mathrm{OH}^{-}\right]$, $\left[\mathrm{NH}_{3}\right]$ and $\left[\mathrm{NH}_{4}^{+}\right]$at equilibrium?
There are two processes occuring:
I. Neutralizaton
$\mathrm{NH}_{3}+\mathrm{HCl}$
$\mathrm{NH}_{4}^{+}+\mathrm{Cl}^{-}$

St $\quad 0.1 \mathrm{M}(1 \mathrm{~L}) \quad 0.02 \mathrm{~L}(1 \mathrm{M})$
0.1 mole 0.02 moles

End: $0.1-.02=.08 \mathrm{~mol} 0$
$0.08 \mathrm{~mole} / 1.02 \mathrm{~L}=0.078 \mathrm{M}$
0.02mol . 02 mol
.02mol/1.02=0196M

## Neutralization

II. The equilibrium between ammonia \& ammonium:
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O}$
St. $\quad 0.078 \mathrm{M}$
End: 0.078-x
$\mathrm{NH}_{4}{ }^{+}(\mathrm{aq}) \quad+$
0.0196 M
$0.0196+x$
$\mathrm{OH}^{-}(\mathrm{aq})$
OM
x
$1.8 \times 10^{-5}=\frac{\left[\left[\mathrm{NH} \rrbracket_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]\right.}{\left[\mathrm{NH}_{3}\right]}=\frac{(0.0196+x)(x)}{0.078-x \longleftarrow} \quad$ You can safely ignore the
$x=\frac{\left(1.8 \times 10^{-5}\right)(0.078)}{0.0196}=7.16 \times 10^{-5}$
$\left[\mathrm{NH}_{3}\right]=0.078 \mathrm{M}$
$\left[\mathrm{NH}_{4}{ }^{+]}=0.0197 \mathrm{M}\right.$

## Buffering.

This is probably the most important part of the section.

We will cover:

1. The common ion effect
2. Buffered solutions
3. Buffering capacity
4. The Henderson-Hassellbach equation
5. Preparing a buffer.

## Buffering.

Buffering is all about controlling pH .
Even if the concentrations are small, large changes in pH can have huge effects on chemical reactions.

In biology, this is particularly critical as the intracellular pH of virtually all cells in nature is around neutral, and significant deviations have profound effects on function.

We'll learn here how to keep pH steady.

## Buffering.

We'll start with an example that shows how buffering works:
Example: What is the pH of a solution of 0.1 M acetic acid $\left(\mathrm{CH}_{3} \mathrm{COH}\right)$ and 0.1 M sodium acetate ( $\mathrm{NaCH}_{3} \mathrm{CO}_{2}{ }^{-}$)?
Start with equilibrium of acetic acid/acetate:

Init:

\[

\]

$K_{a}=1.8 \times 10^{-5}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}=\frac{(0.1+x)(x)}{(0.1-x)}$

Will $x$ be small? What are you comparing it to?

## Buffering.

Example problem: consisting of 0.1 M acetic acid $\left(\mathrm{CH}_{3} \mathrm{COH}\right)$ and 0.1 M sodium acetate $\left(\mathrm{NaCH}_{3} \mathrm{CO}_{2}{ }^{-}\right)$

$$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5} \\
& \text { Init: } 0.1 \text { mole } 0.1 \text { mole } 0 \\
& \text { final: } 0.1-\mathrm{x} \quad 0.1+\mathrm{x} \quad \mathrm{x} \\
& K_{a}=1.8 \times 10^{-5}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}=\frac{(0.1+x)(x)}{(0.1-x)}
\end{aligned}
$$

Will $x$ be small? What are you comparing it to?
$1.8 \times 10^{-5}$ is a lot smaller than 0.1 , so x has to be small compared to 0.1 .

$$
1.8 \times 10^{-5}=\frac{0.1(x)}{0.1}=x: p H=-\log \left(1.8 \times 10^{-5}\right)=4.74
$$

## Buffering.

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}
$$

## Common ion effect

Manifestation of LeChatlier's principle
Common ion effect: Adding a reagent that contains an ion already at equilibrium in solution will push the equilibrium the other direction.
Here, adding $\mathrm{H}_{3} \mathrm{O}^{+}$pushes the equilibirum to left, absorbing acid.
If both acetate and acetic acid are added to a solution, changes in pH will be resisted in both directions.
Added acid will be absorbed by acetate.
Added base will be absorbed by acetic acid.

## Buffering.

Example: What is the pH of the solution after addition of 10 mL of 1 M HCl (to 1 L )?

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}
$$

| Init: | 0.1 mole | 0.1 mole | $1.8 \times 10^{-5}$ |
| :--- | :--- | :--- | :--- |
| change: | $0.1+.01=0.11$ mole | $0.1-.01=.09$ |  |
| equilib: | $.11 / 1.01 \mathrm{~L}-\mathrm{x}$ | $0.09 / 1.01 \mathrm{~L}+\mathrm{x}$ | x |

$1.8 \times 10^{-5}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}=\frac{(0.09 / 1.01 L+x)(x)}{(0.11 / 1.01 L-x)}=\frac{.09 x}{.11}$
$x=\frac{.11}{.09}\left(1.8 \times 10^{-5}\right)=2.2 \times 10^{-5}$
$p H=-\log \left(2.2 \times 10^{-5}\right)=4.66$
Lets compare the result of adding 10 mL of 1 M HCl to 1 L without the buffer:
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{0.01 \mathrm{~L}\left(1 \mathrm{M}_{3} \mathrm{O}^{+}\right)}{1.01 \mathrm{~L}}=9.9 \times 10^{-3} \mathrm{pH}=-\log \left(9.9 \times 10^{-3}\right)=2.00$

## Buffering.

$1.8 \times 10^{-5}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}=\frac{(0.09 / 1.01 L+x)(x)}{(0.11 / 1.01 L-x)}=\frac{.09 x}{.11}$
$x=\frac{.11}{.09}\left(1.8 \times 10^{-5}\right)=2.2 \times 10^{-5}$
$p H=-\log \left(2.2 \times 10^{-5}\right)=4.66$
Lets compare the result of adding 10 mL of 1 M HCl to 1 L without the buffer:
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{0.01 \mathrm{~L}\left(1 \mathrm{MH}_{3} \mathrm{O}^{+}\right)}{1.01 \mathrm{~L}}=9.9 \times 10^{-3} \mathrm{pH}=-\log \left(9.9 \times 10^{-3}\right)=2.00$

## Buffer:

$\Delta \mathrm{pH}=.08$

| 4.74 |  |
| :--- | :--- |
|  |  |
|  | +10 mL <br> 1 M HCl |

No Buffer:
$\Delta \mathrm{pH}=5.0$ !


## Buffering.

Now, let's go the opposite way and see what happens when we add base, for example 20 mL of 1 M NaOH .

```
    \(\mathrm{NaOH} \longrightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}\)Full dissociation.
    .02-. 02 . 02 . 02
    \(\mathrm{OH}^{-}+\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O}(\mathrm{aq})\)
st. . \(02 \mathrm{~mol} .1 \mathrm{~mol} . \quad 1 \mathrm{~mol}\)
eq. \(0 \quad .1-.02=.08 \mathrm{~mol} \quad .1+.02=0.12 \mathrm{~mol}\)
    \(\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\)
Init: .08 mole 0.12 mole
change: -x
equilib: . \(08 / 1.02-\mathrm{x}\)
\(+x \quad+x\)
    \(.12 / 1.02+\mathrm{x} \quad \mathrm{x}\)
```


## Buffering.

Now, let's go the opposite way and see what happens when we add base, for example 20 mL of 1 M NaOH .

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}
$$

| Init: | .08 mole | 0.12 mole |  |
| :--- | :--- | :---: | :--- |
| change: | -x | +x | +x |
| equilib: | $.08 / 1.02-\mathrm{x}$ | $.12 / 1.02+\mathrm{x}$ | x |

$$
\begin{aligned}
& 1.8 \times 10^{-5}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]}=\frac{(0.12 / 1.02 L+x)(x)}{(0.08 / 1.02 L-x)}=\frac{.12 x}{.08} \\
& x=\frac{.08}{.12}\left(1.8 \times 10^{-5}\right)=1.2 \times 10^{-5} \\
& p H=-\log \left(1.2 \times 10^{-5}\right)=4.92
\end{aligned}
$$

Note, in both of these cases where the buffer is working, there is still plenty of both acetate and acetic acid. If one runs out, the buffer will not work anymore. If acetate runs out, there is only acetic acid and only base can be buffered. If acid runs out, only acid can be buffered.

## The Henderson Hasselbach equation

All this can be summarized with a very convenient equation, the Henderson Hasselbach equation. It is a favorite tool of biochemists.
$\mathrm{HA}+\mathrm{H}_{2} \mathrm{O}=\mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$K_{a}=\frac{\left[A^{-}\right]\left[H_{3} O^{+}\right]}{[H A]}$
$-\log K_{a}=-\log \left[H_{3} \mathrm{O}^{+}\right]-\log \left\{\frac{\left[A^{-}\right]}{[H A]}\right\}$
$p K_{a}=p H-\log \left\{\frac{\left[A^{-}\right]}{[H A]}\right\}$

The pH of any buffer can be known with the $\mathrm{pK}_{\mathrm{a}}$ of weak acid \& concentrations of HA and $\mathrm{A}^{-}$
the pH of a buffer system is

Centered on $\mathrm{pK}_{\mathrm{a}}$ of weak acid

## The blood carbonate buffer system

Example: Carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$, and it's conjugate base, $\mathrm{HCO}_{3}^{-}$, are responsible for maintaining the pH of blood at 7.40. Calculate the ratio of the two conjugate partners necessary to establish a buffer of $\mathrm{pH}=7.4$.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O}=\mathrm{HCO}_{3}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=8.0 \times 10^{-7} \text { at } 37^{\circ} \mathrm{C} \\
& p H=p K_{a}+\log \left\{\frac{\left[A^{-}\right]}{[\mathrm{HA}]}\right\} \\
& p H=p K_{a}+\log \left\{\frac{\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}\right\} \\
& 7.4=-\log \left(8.0 \times 10^{-7}\right)+\log \left\{\frac{\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO} 3\right]}\right\} \\
& 7.4=6.10+\log \left\{\frac{\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}\right\} \\
& 1.3=\log \left\{\frac{\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}\right\} \quad \text { In blood, the arterial concentrations are: }\left[\mathrm{HCO}_{3}^{-]}=0.024 \mathrm{M}\right. \\
& {\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=0.0012 \mathrm{M}} \\
& 10^{1.3}=\frac{\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}=20
\end{aligned}
$$

## Buffer Design

Design a buffer system for a pH of 7.5.
Let's use phosphate. For a pH of 7.5 , we need a pKa in the right range: $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HPO}_{4}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \mathrm{K}_{\mathrm{a}}=6.2 \times 10^{-8}$
$-\log \left(6.2 \times 10^{-8}\right)=7.27$, so close to 7.5 .
$p H=p K_{a}+\log \left\{\frac{\left[A^{-}\right]}{[H A]}\right\}$
$p H=p K_{a}+\log \left\{\frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}\right\}$
$7.5=-\log \left(6.2 \times 10^{-8}\right)+\log \left\{\frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}\right\}$
$7.5=7.21+\log \left\{\frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}\right\}$
$0.29=\log \left\{\frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}\right\}$
$10^{0.29}=\frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}=1.96$
Note: When the concentrations of $\mathrm{HA}=\mathrm{A}$ :
$p H=p K a+\log \frac{\left[A^{-}\right]}{[H A]}=p K a+\log 1=p K a$
The $\mathrm{pH}=\mathrm{pKa}$

A 2:1 molar ratio of $\mathrm{Na}_{2} \mathrm{HPO}_{4}: \mathrm{NaH}_{2} \mathrm{PO}_{4}$ will give you a $\mathrm{pH}=7.5$.

