

## Le Chatelier's

Princ. at Work every day!

Effect of acid rain on erosion of limestone/marble Calcite--- $\mathrm{CaCO}_{3(\mathrm{~s})}<----->\mathrm{Ca}^{+2}+\mathrm{CO}_{3}{ }^{-2}$

$$
\mathrm{CO}_{3}^{-2}+\mathrm{H}^{+}<----->\mathrm{HCO}_{3}^{-}
$$

acid rain---shifts calcite equilibrium to right!

Tooth decay--same princple (now acid from lactic acid--produced by bacteria---degrades hydroxyapatite):

$$
\mathrm{Ca}_{10}\left(\mathrm{PO}_{4}\right)_{6}(\mathrm{OH})_{2}+14 \mathrm{H}^{+}<--->10 \mathrm{Ca}^{+2}+6 \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+2 \mathrm{H}_{2} \mathrm{O}
$$

## Polyprotic acids/bases---Chapter 10 ECA

$$
\mathrm{HA}<---->\mathrm{H}^{+}+\mathrm{A}^{-} \quad \mathrm{pK}_{1}
$$

$$
\mathrm{H}_{2} \mathrm{~A}<---->\mathrm{H}^{+}+\mathrm{HA}^{-}<----->\mathrm{H}^{+}+\mathrm{A}^{-2} ; \mathrm{pK}_{1} \text { and } \mathrm{pK}_{2}
$$

$$
\mathrm{H}_{3} \mathrm{~A}<---->\mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{~A}^{-2}<--->\mathrm{HA}^{-2}+\mathrm{H}^{+}<---->\mathrm{A}^{-3}+\mathrm{H}^{+} ; \mathrm{pK}_{1}, \mathrm{pK}_{2}, \mathrm{pK}_{3}
$$

- Can have also species where acidic protons come as a result of amine sites----so with proton---site is + charge---loss of proton gives neutral species: $\mathrm{RNH}_{3}{ }^{+}<-------\mathrm{RNH}_{2}+\mathrm{H}^{+} \quad \mathrm{pK}_{\mathrm{a}}$
-Can have combination of both types of protonated sites in same structure--Amino acids!



Zwitterion

Let's look at a real amino acid---which is triprotic---three different $\mathrm{pK} \mathrm{a}_{\mathrm{a}}$ values---

$$
\mathrm{A}^{2-}
$$

These systems are more complex
from a titration standpoint---and also to calculate the pH , given a specific concentration of one form of the molecule!
$\mathrm{K}_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{b}}$ relationships for such species---

$\mathrm{HA}^{-}+\mathrm{H}_{2} \mathrm{O}<----->\mathrm{H}_{2} \mathrm{~A}+\mathrm{OH}^{-} \mathrm{K}_{\mathrm{b} 2}$-the weaker conjugate base
$\mathrm{H}_{2} \mathrm{O}$ <----------> $\mathrm{H}^{+}+\mathrm{OH}^{-} \mathrm{K}_{\mathrm{w}}$
therefore: $K_{a 1} K_{b 2}=K_{w}$
stronger

$$
\begin{array}{cc}
H \mathrm{~A}^{-}<-\cdots-\cdots>\mathrm{H}^{+}+\mathrm{A}^{-2} & \mathrm{~K}_{\mathrm{a} 2} \\
\mathrm{~A}^{-2}+\mathrm{H}_{2} \mathrm{O}<-\cdots-\cdots \mathrm{HA}^{-}+\mathrm{OH}^{-} & \mathrm{K}_{\mathrm{b} 1}
\end{array}
$$

conj.
base therefore: $\mathbf{K}_{\mathrm{a} 2} \mathbf{K}_{\mathrm{b} 1}=\mathbf{K}_{\mathbf{w}}$
Similarly---can derive--relationships for triprotic system:

$$
K_{a 1} K_{b 3}=K_{w} ; K_{a 2} K_{b 2}=K_{w} ; \text { and } \quad K_{a 3} K_{b 1}=K_{w}
$$

Diprotic case in more detail---what is pH of solution?---let's use simple diprotic amino acid as generic example:
$\mathrm{H}_{3} \mathrm{~N}^{+} \mathrm{C}(\mathrm{R}) \mathrm{COOH}$ <------> $\mathrm{H}_{3} \mathrm{~N}^{+} \mathrm{C}(\mathrm{R}) \mathrm{COO}^{-}$-------> $\mathrm{H}_{2} \mathrm{NC}(\mathrm{R}) \mathrm{COO}^{-}$

$$
\underset{\mathrm{pK}_{\mathrm{a} 1}=2.329}{\mathrm{H}_{2} \mathrm{~L}^{+}<--------->} \quad \mathrm{HL} \underset{\mathrm{pK}_{\mathrm{a} 2}=9.747}{<------------\gg} \mathrm{L}^{-}
$$

$$
\text { thus---- } \mathrm{L}^{-}+\mathrm{H}_{2} \mathrm{O} \text { <----> } \mathrm{HL}+\mathrm{OH}^{-} \quad \mathbf{K}_{\mathbf{b} 1}
$$

$$
\mathrm{HL}+\mathrm{H}_{2} \mathrm{O}<----->\mathrm{HL}^{+}+\mathrm{OH}^{-} \quad \mathbf{K}_{\mathrm{b} 2}
$$

What is pH of solution of $\mathrm{H}_{2} \mathrm{~L}^{+}$salt--at 0.05 M ?
$\mathrm{pK}_{\mathrm{a} 1}=\mathrm{pK}_{1}=2.329 ; \mathrm{K}_{\mathrm{a}}=4.69 \times 10^{-3}$
HL is much weaker acid--- $\mathrm{K}_{\mathrm{a}}=1.79 \times 10^{-10}---$
So-- $\mathrm{H}_{2} \mathrm{~L}^{+}$will dissociate slightly to generate $\mathrm{H}^{+}$in solution--but the contribution by further dissociation of $\mathrm{HL}<--->\mathrm{H}^{+}$is negligible
so pH can be calculated treating $\mathrm{H}_{2} \mathrm{~L}^{+}$as monoprotic acid--
$\mathrm{K}_{1}=\mathrm{x}^{2} /(\mathrm{F}-\mathrm{x}) ; \mathrm{F}=0.05 \mathrm{M} ; \mathrm{x}=1.31 \times 10^{-2} \mathrm{M}=[\mathrm{HL}]=\left[\mathrm{H}^{+}\right]$
Therefore: $\mathbf{p H}=-\log \left(\mathbf{1 . 3 1 \times 1 0 ^ { - 2 }}\right)=\mathbf{1 . 8 8}$
What is concentration of $\mathrm{L}^{-}$in such a solution?
We know that $\mathrm{K}_{2}=\left(\left[\mathrm{L}^{-}\right]\left[\mathrm{H}^{+}\right]\right) /[\mathrm{HL}] ;\left[\mathrm{L}^{-}\right]=\left(\mathrm{K}_{2}[\mathrm{HL}]\right) /\left[\mathrm{H}^{+}\right]$
$\left[L^{-}\right]=\left(1.79 \times 10^{-10}\right)\left(1.31 \times 10^{-2}\right) /\left(1.31 \times 10^{-2}\right)=\mathbf{1 . 7 9} \times \mathbf{1 0}^{-10} \mathbf{M}=\mathrm{K}_{2}$
as long as $K_{1}>K_{2}$ by at least 1-2 orders of magnitude---the assumption to neglect second dissociation reaction in calculating proton concentration is OK!

If solution contained $\mathrm{L}^{-}$only at 0.05 M to start--what would be pH ?
weak base problem---Need $\mathrm{K}_{\mathrm{b} 1}$ value $; \mathbf{K}_{\mathrm{b} 1}=\mathbf{K}_{\mathbf{w}} / \mathbf{K}_{\mathbf{2}}=\mathbf{5 . 5 9} \times 10^{-5}$
$\mathrm{OH}^{-}$produced from small amount of HL that forms would be negligible--since $\mathrm{K}_{\mathrm{b} 2}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{1}=10^{-14} / 4.69 \times 10^{-3}=2.13 \times 10^{-12}$----very very weak base!

So pH is based only on $\mathrm{K}_{\mathrm{b} 1}$ value:

$$
\begin{aligned}
\mathrm{K}_{\mathrm{b} 1}=\mathrm{x}^{2} / \mathrm{F}-\mathrm{x} ; 5.59 \times 10^{-5}=\mathrm{x}^{2} /(0.05-\mathrm{x}) ; \mathrm{x}=4.84 \times 10^{-2} \mathrm{M} & =\left[\mathrm{OH}^{-}\right] \\
& =[\mathrm{HL}]
\end{aligned}
$$

$$
\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{OH}^{-}\right]=10^{-14} / 4.84 \times 10^{-2}=6.08 \times 10^{-12} \mathrm{M}
$$

$$
\text { therefore: } \mathbf{p H}=\mathbf{1 1 . 2 2}
$$

Finally--what about a 0.05 M solution of HL --What is pH ? more complex--since HL is intermediate form--it can be both a base and acid (an amphiprotic species!!!!)

$$
\begin{array}{cl}
\mathrm{HL}<------>\mathrm{H}^{+}+\mathrm{L}^{-} & \mathrm{K}_{2}=1.79 \times 10^{-10} \\
\mathrm{HL}+\mathrm{H}_{2} \mathrm{O}<----->\mathrm{H}_{2} \mathrm{~L}^{+}+\mathrm{OH}^{-} & \mathrm{K}_{\mathrm{b} 2}=2.13 \times 10^{-12} \\
\text { since } \mathrm{K}_{2}>\mathrm{K}_{\mathrm{b} 2} ; \text { expect solution of } \mathrm{HL} \text { to be acidic! }
\end{array}
$$

Determing pH of solution containing HL alone--is perfect example of solving more complex simultaneous equilibria type problems in chemistry!
best starting point---use "charge balance" equation
must have charge neutrality in solution--therefore the total concentration of all positively charged species = total concentration of all negatively charged species in solution!

$$
\left[\mathrm{H}^{+}\right]+\left[\mathrm{H}_{2} \mathrm{~L}^{+}\right]=\left[\mathrm{L}^{-}\right]+\left[\mathrm{OH}^{-}\right]
$$

or $\left[\mathrm{H}_{2} \mathrm{~L}^{+}\right]-\left[\mathrm{L}^{-}\right]+\left[\mathrm{H}^{+}\right]-\left[\mathrm{OH}^{-}\right]=0$
but we have relationships that we can substitute for each of these species:

$$
\frac{[H L]\left[H^{+}\right]}{K_{1}}-\frac{[H L] K_{2}}{\left[H^{+}\right]}+\left[H^{+}\right]-\frac{K_{w}}{\left[H^{+}\right]}=0
$$

Can solve for $\left[\mathrm{H}^{+}\right]$(see ECA--p. 217)

$$
\left[H^{+}\right]=\sqrt{\frac{K_{1} K_{2}[H L]-K_{1} K_{w}}{K_{1}+[H L]}}
$$

everything is known except [HL]-----but we know that while HL is both an acid and base--it is weak--and hence the concentration of [HL] at equilibrium is going to be very close to the formal concentration that you add to the solution--F; thus:

$$
\left[H^{+}\right]=\sqrt{\frac{K_{1} K_{2} F-K_{1} K_{w}}{K_{1}+F}}
$$

recall we said that
$\mathrm{F}=0.05 \mathrm{M}$ to start!
$\mathrm{K}_{1} \mathrm{~K}_{\mathrm{w}}$ is usually $\lll \mathrm{K}_{1} \mathrm{~K}_{2} \mathrm{~F}$; and $\mathrm{K}_{1} \ll \mathrm{~F}$

$$
\left[H^{+}\right]=\sqrt{\frac{K_{1} K_{2} F-K_{1} K_{w}}{K_{1}+F}} \longrightarrow\left[H^{+}\right]=\sqrt{K_{1} K_{2}}
$$

take log of both sides:

$$
\begin{aligned}
& \log \left[\mathrm{H}^{+}\right]=1 / 2 \log \left(\mathrm{~K}_{1} \mathrm{~K}_{2}\right) \\
& \log \left[\mathrm{H}^{+}\right]=1 / 2\left(\log \mathrm{~K}_{1}+\log \mathrm{K}_{2}\right) \\
& \text { multiply by sides by }-1: \\
& -\log \left[\mathrm{H}^{+}\right]=1 / 2\left(-\log \mathrm{K}_{1}-\log \mathrm{K}_{2}\right) \\
& \mathbf{p H}=\mathbf{1} / \mathbf{2}\left(\mathbf{p} \mathbf{K}_{\mathbf{1}}+\mathbf{p} \mathbf{K}_{\mathbf{2}}\right)
\end{aligned}
$$

so the pH of the solution of $0.05 \mathrm{M} \mathrm{HL}=1 / 2(2.329+9.747)$

$$
\mathrm{pH}=6.04
$$

note---pH of the HL solution is independent of concentration!
once you know the $\mathrm{pH}--$-you can then go back and calculate how much of $\mathrm{H}_{2} \mathrm{~L}^{+}$and $\mathrm{L}^{-}$from the equilibrium constant expressions!
turns out that the concentrations are very low ----approx. $10^{-5} \mathrm{M}$ compared to 0.05 M of HL that was added to solution!

## Example---what is pH of 0.05 M KHP?



## Principal species in solution?

reported as $\alpha$ values vs. pH of solution!----where $\alpha$ is the fraction of total polyprotic acid in a given form---
can estimate $\alpha$ values from log term in HH equation----if ratio is $10 ;(\log (10 / 1)--$-then base form is approx. $90 \%$ fraction---if $\log (100 / 1)$ then base form is $99 \%$ fraction!


$$
\begin{aligned}
& \text { Monoprotic system } \\
& \mathrm{pH}=\underset{\uparrow}{\mathrm{p} K_{1}}+\log \left(\frac{\left[\mathrm{HA}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{~A}\right]}\right) \\
& \text { Diprotic system } \\
& \mathrm{pH}=\underset{\uparrow}{\mathrm{p} K_{2}}+\log \left(\frac{\left[\mathrm{A}^{2-}\right]}{\left[\mathrm{HA}^{-}\right]}\right) \\
& \text {Triprotic system } \\
& \leftarrow \begin{array}{c}
\text { More } \\
\text { acidic }
\end{array} \quad \mathrm{pH} \quad \begin{array}{l}
\text { More } \\
\text { basic }
\end{array} \rightarrow \\
& \mathrm{pH}=\frac{1}{2}\left(\mathrm{p} K_{1}+\mathrm{p} K_{2}\right) \\
& {\left[\mathrm{H}_{2} \mathrm{~A}\right]=\left[\mathrm{A}^{2-}\right]}
\end{aligned}
$$

## Blood-Gas Transfer During Respiration

$\mathrm{CO}_{2}$ when dissolved in solution forms very important polyprotic acid Carbonic Acid--$\mathrm{H}_{2} \mathrm{CO}_{3}$


$$
\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}<----->\mathrm{H}_{2} \mathrm{CO}_{3} \underset{\mathrm{pK}_{1}=6.35}{<---->} \mathrm{HCO}_{3}^{-}+\mathrm{H}^{+}<---->\mathrm{CO}_{3}^{-2}+\mathrm{H}^{+}
$$

controls pH of blood--- If your lungs are not working well to get rid of $\mathrm{CO}_{2}---$ pH of blood decreases (more carbonic acidpresent)

In clinical labs they measure $\mathrm{P}_{\mathrm{CO} 2}=$ partial pressure of $\mathrm{CO}_{2}$ in blood and also total $\mathrm{CO}_{2}$ species---sum of $\left[\mathrm{CO}_{2}\right]+\left[\mathrm{HCO}_{3}^{-}\right]\left(\mathrm{CO}_{3}^{-2}\right.$-too low to contribute appreciably to total carbon dioxide species present)!

How to measure?---use $\mathrm{CO}_{2}$ sensor---

$\mathrm{CO}_{2}$ sensors: Optical


$$
\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$



$$
\mathrm{pK}_{1}=6.35 \quad \mathrm{pK}_{2}=10.33
$$

fluorescent indicator is sensitive to pH

$$
\begin{aligned}
& \mathrm{HIn} \quad \longleftrightarrow \quad \mathrm{In}^{-} \quad \lambda_{\max }=625 \mathrm{~nm} \\
& \lambda_{\max }=545 \mathrm{~nm} \\
& \text { gred }
\end{aligned}
$$

What is the $\mathrm{pK}_{\mathrm{A}}$ of the indicator?
pI values---- pH of solution where polyprotic species is neutral! called isoelectric pH value!




Arginine (Arg)
$\mathrm{pK}_{1}=1.82$
$\mathrm{pK}_{2}=8.99$
$\mathrm{pK}_{3}=12.48$
neutral zwitterion

$$
\mathrm{pI}=10.74
$$

Average of $\mathrm{pK}_{2}, \mathrm{pK}_{3}$



Titration of diprotic acid with strong base---shape depends on values of $\mathrm{pK}_{1}$ and $\mathrm{pK}_{2}$

for all curves-$\mathrm{pK}_{1}=4.00$
solid black line$\mathrm{pK}_{2}=6$
red line
$\mathrm{pK}_{2}=8$
dashed line $\mathrm{pK} 2=10$
assume 50 mL of $0.02 \mathrm{M} \mathrm{H}_{2} \mathrm{~A}$ to starttitrated with 0.1 M NaOH
titration of 50 mL of $0.02 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ with 0.1 M HCl


