Compare:

- Weak acid $\mathrm{HNO}_{2}$ : pH of 0.10 M solution $=2.17$

Let's compare the pH of the weak nitrous acid with the pH of a strong acid like nitric acid:

$$
0.10 \mathrm{mHNO}_{3} \text {, what is } \mathrm{pH}_{1} \text { ? }
$$

$$
\begin{aligned}
\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{O} & \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{NO}_{3} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\left[\mathrm{HNO}_{3}\right]_{\text {nominal }}=0.10 \mathrm{~m} \\
\mathrm{PH} & =1.00
\end{aligned}
$$

The stronger the acid:

- the lower the pH of a solution of given concentration will be
- the higher the concentration of hydronium ion (when compared to the nominal acid concentration)
${ }^{145}$ Consider an 0.100 M solution of the weak base ammonia:

$$
\mathrm{NH}_{3} j \mathrm{~K}_{b}=1.8 \times 10^{-5}\left(p \mathrm{~A}-14,6 b b i n g 9^{\text {th }}\right)
$$

What is the pH ?

$$
\begin{aligned}
& \text { at is the pH? } \\
& \mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \underset{\text { Make a chart. We're interested in solving for }}{=} \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-} \mathrm{K}_{b}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}=1.8 \times 10^{-\mathrm{S}} .
\end{aligned}
$$ HYDROXIDE concentration since it relates to $\mathrm{pH} . .$.

| Species | [Initial $]$ | $\Delta$ | $\left[\epsilon_{\text {quilibrium }}\right]$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{NH}_{4}+$ | $O$ | $+X$ | $X$ |
| $\mathrm{OH}^{-}$ | $O$ | $+X$ | $X$ |
| $\mathrm{NH}_{3}$ | 0.100 | $-X$ | $0.100-X$ |

Let "x" equal the change in ammonium ion concentration.

$$
\begin{aligned}
& \frac{(x)(x)}{0.100-x}=1.8 \times 10^{-5} \\
& \frac{x^{2}}{0.100-x}=1.8 \times 10^{-5}
\end{aligned}
$$

146

$$
p H=11.13
$$

*If you'd solved this via the quadratic formula, the answer would've been $\mathrm{pH}=11.13$

$$
\begin{aligned}
& \frac{x^{2}}{0.100-x}=1.8 \times 10^{-5} \\
& \text { We can solve using the quadratic } \\
& \text { equation, but ... } \\
& \downarrow \begin{array}{l}
x<c 0.100,50 \\
0.100-x=0.100
\end{array} \\
& \frac{x^{2}}{0.100}=1.8 \times 10^{-5} \\
& x=0.0013416408 m=\left[\mathrm{OH}^{-}\right] \text {(see chart on prev, page) } \\
& \text { oOH }=2.8) \quad\left(\text { oOH }=-\log \left[\mathrm{OH}^{-}\right]\right) \\
& \rho H+2,8)=14,00 \quad(p H+p u H=14,00)
\end{aligned}
$$

Compare pH to the pH of an 0.100 M solution of the strong base NaOH : $\mathrm{pH}_{\mathrm{NH}_{3}}=11.13$

$$
\begin{aligned}
& \mathrm{NaOH}_{a} \rightarrow \mathrm{Na}^{+}+\partial H^{-} \\
& {\left[\mathrm{OH}^{-}\right] }=[\mathrm{NaOH}]_{\text {nominal }}=0.100 \mathrm{M} \\
& \mathrm{POH}=1.00 \\
& \mathrm{PH}=13.00
\end{aligned}
$$

The stronger the base:

- the higher the pH will be for a solution of given concentration
- the higher the HYDROXIDE concentration (compared to the nominal base concentration)
${ }^{44}$ Find the pH and the degree of ionization for an 0.10 M solution of formic acid: HCHO

$$
\mathrm{HCHO} 2+\mathrm{H}_{2} \mathrm{O} \stackrel{\rightharpoonup}{\rightleftharpoons} \mathrm{HO}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} ; \mathrm{K}_{a}=\left[\mathrm{CHO}_{2}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.7 \times 10^{-4}
$$

Let's set up an equilibrium chart so we can find hydroniumn ion $\left[\mathrm{HCHO}_{2}\right]$ (value from concentration

| Species | [Initial $]$ | $\Delta$ | $[$ Equilibrium $]$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}_{3} \mathrm{O}^{+}$ | 0 | $+X$ | $X$ |
| $\mathrm{CHO}_{2}^{-}$ | 0 | $+X$ | $X$ |
| $\mathrm{HCHO}_{2}$ | 0,10 | $-X$ | $0.10-X$ |

Let "x' equal the change in hydronium ion concentration

$$
\begin{aligned}
& \frac{(x)(x)}{0.10-x}=1.7 \times 10^{-4} \\
& \frac{x^{2}}{0.10-x}=1.7 \times 10^{-4} \\
& \sqrt{x<c} 0.10 \\
& \frac{x^{2}}{0.10-x}=1.7 \times 10^{-4}
\end{aligned}
$$

$$
x=0.0041231058 \mathrm{~m}=\left[\mathrm{H}_{3}{ }^{+}{ }^{+}\right]
$$

$$
p H=2.38 \quad\left(\rho H=-1 v_{y}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\right)
$$

${ }^{149}$ What is degree of ionization? It's the fraction of a weak acid or base that ionizes in solution.

$$
\begin{aligned}
& \text { DOL }=\frac{\left[\mathrm{CHO}_{2}^{-}\right]}{\left[\mathrm{H}\left(\mathrm{HO}_{2}\right]\right. \text { nominal }}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{HCHO} \mathrm{HO}_{2}\right] \text { nominal }} \\
& \frac{0.0041231058 \mathrm{M}}{0.10 \mathrm{~m}}=0.041=\mathrm{DOI}
\end{aligned}
$$

Often we express DOI as a percentage, called "percent ionization".

$$
0 / 010 n i z a t i o n=00 I \times 100=4.1 \% \text { Ionized }
$$

When you do Experiment 16A. By Le Chateleir's Principle, adding water to the equilibrium should force it to the right - meaning that more acid will ionize - even as the pH goes up!. Therefore, the degree of (or percent) ionization should INCREASES as the concentration of the acid DECREASES. Check this with your experiment 16A data on acetic acid.

150
An aqueous solution of 0.25 M trimethylamine has a pH of 11.63. What's the experimental value of Kb?

$$
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons\left(\mathrm{(H}_{3}\right)_{3} \mathrm{NH}^{+}+\mathrm{OH}^{-} \mathrm{K}_{6}=\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NH}^{+}\right][\mathrm{OH}]
$$

For now, let's make an equilibrium chart like we've done for the $\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}\right]$ other weak acid/base problems.


Let "x" equal the change in hydroxide concentration

$$
\frac{x^{2}}{0.25-x}=t b
$$

At this point, we need to find out what "x" is ... but we cant find it from THIS equation.

151

$$
\frac{x^{2}}{0.25-x}=t_{b}
$$

SInce we know pH, we can use it to find "x". "x" is hydroxide concentration. First. let's use pH to find pOH .

$$
\begin{aligned}
& \text { pH =11.63 } \\
& \begin{array}{l}
11.63+\rho O H=14.00 \quad(\rho H+\rho U H=14.00) \\
\text { pOH }
\end{array}=2.37 \\
& {[\text { OH H }]=x=10^{-2.3)} \quad\left([04-]=10^{-p 04}\right)} \\
& x=0.0042657852
\end{aligned}
$$

Plug "x" back into the expression for Kb, and we've got Kb.

$$
\frac{(0.0042657952)^{2}}{0.25-0.0042657952}=166=7.4 \times 10^{-5}
$$

SALTS

- Compounds that result from the reaction of an acid and a base.
- Salts are strong electrolytes (completely dissociate in water) IF SOLUBLE (not all salts dissolve appreciably).
- Most ionic compounds are considered salts (they can be made by some reaction between the appropriate acid and base)
- Salts have acidic and basic properties! The ions that form when salts are dissolved can be acidic, basic, or neutral.
- Salts made from WEAK ACIDS tend to form BASIC solutions
- Salts made from WEAK BASES tend to form ACIDIC solutions

$$
\mathrm{Na}_{2} \mathrm{CO}_{3}: \mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow 2 \mathrm{Na}^{+}+\mathrm{CO}_{3}^{2-}
$$

Do any of these ions have acidic or basic properties?
$\mathrm{Na}^{+}$: neutral. Not a proton donor or a proton acceptor
$\mathrm{CO}_{3} \mathrm{CO}^{2-}$ : BASIC, since it can accept protons to form the weak acid CARBONIC ACID

$$
\mathrm{H}_{2} \mathrm{CO}_{3} \mathrm{ACID}^{t} \mathrm{H}_{2} \mathrm{O} \rightleftharpoons 2 \mathrm{H}_{3} \mathrm{O}_{\mathrm{BASE}}^{t}+\mathrm{CO}_{3}^{-2}
$$

ex: $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$


For this reaction to occur, HA MUST be stable in water. In other words, a weak acid.
$\qquad$ The anion is a BASE. It can accept a proton from water to form the weak (therefore stable as a molecule!) acid HA

$$
\left.K_{b}=\frac{[\mathrm{HA}]\left[\mathrm{OH}^{-}\right]}{\left[A^{-}\right]} \right\rvert\, \text {This is the base ionization constant for } A^{-}
$$

Since $\bar{A}$ and HA are a conjugate pair, the ionization constants are related! You will generally not find both

$$
\begin{aligned}
& K_{w}=\left(K_{a, H A}\right)\left(K_{b, A^{-}}\right) \\
& 1.0 \times 10^{-14} \\
& \quad L_{1}=p K_{n}+p K_{b}
\end{aligned}
$$ the Ka AND Kb for a conjugate pair in the literature, since one can be easily converted to the other!

## SALT OF A WEAK BASE

ex: $\mathrm{NH}_{4} \mathrm{Cl}$

$$
\begin{aligned}
& \mathrm{BHCl} \longrightarrow \mathrm{BH}^{+}+\mathrm{Cl}^{-} \mathrm{I}^{-} \text {The sql dissociates completely! }
\end{aligned}
$$

$$
\begin{aligned}
& \left.K_{a}=\frac{[\mathrm{B}]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{BH}^{+}\right]} \right\rvert\, \text {Acid ionization constant for } \mathrm{BH}^{+} \\
& \underset{1,0 \times 10^{-1 / 4}}{k_{a, B H^{t}}}=\left(K_{b, B}\right)
\end{aligned}
$$

Find the pH for salt solutions just like you would find pH for any other weak acid or weak base solutions. Only trick is to find out whether the salt is actually acidic or basic!
$0.100 \mathrm{MN} \mathrm{NH} C l \ldots$ Find the pH of the solution

$$
\begin{aligned}
& \mathrm{NH}_{4} \mathrm{LI} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{Cl}^{-} \text {is the salt acidic, basic, or neutral? Look at the } \\
& \text { IONS the salt releases when it dissolves! } \\
& \mathrm{NH}_{4}{ }^{+}: \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \text {since ammonia is a WEAK base, } \text { that means it will exit in water as } \\
& \text { molecules ... meaning the reaction } \\
& \text { we wrote can occur and ammonium } \\
& \text { ion can act as an acid. } \\
& \mathrm{Cl}^{-}: \mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCl}+\mathrm{OH}^{-}
\end{aligned}
$$

So the equilibrium we'll need to look at is the one with the acidic ammonium ion.

$$
\begin{aligned}
& \mathrm{NH}_{4}++\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}+\left\lvert\, \mathrm{K}_{\mathrm{a}_{1} \mathrm{NH}_{4}}+=\begin{array}{l}
\text { Well need to find } \mathrm{Ka} \text { for } \\
\text { ammonium by looking at } \mathrm{Kb} \text { for } \\
\text { its conjugate, ammonia. }
\end{array}\right. \\
& K_{a}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3 \mathrm{O}^{+}}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}=\text {? } \\
& K_{b, \mathrm{NH}_{3}}=1.8 \times 10^{-5} \quad(\mathrm{pA}-14) \\
& K_{a} \times K_{b}=1.0 \times 10^{-14} \\
& \mathrm{Ka}_{a, \mathrm{NH}_{4}}+=5.56 \times 10^{-10}
\end{aligned}
$$

${ }^{156} \mathrm{NH}_{4}++\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} ; \mathrm{Ka}=\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.56 \times 10^{-10}$ Set up and solve this equilibrium like any other weak acid $\left[\mathrm{NH}_{4}+\right]$
problem!

| Species | [Initial] | $\Delta$ | [Equllbtium $]$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{NH}_{3}$ | 0 | $+X$ | $x$ |
| $\mathrm{H}_{3} \mathrm{O}^{+}$ | 0 | $+x$ | $X$ |
| $\mathrm{NH}_{4}{ }^{+}$ | 0.100 | $-x$ | $0.100-x$ |

Let "x" equal the change in ammonia concentration...

$$
\begin{aligned}
& \frac{(x)(x)}{(0.100-x)}=5.56 \times 10^{-10} \\
& \frac{x^{2}}{0.100-x}=5.56 \times 10^{-10} \\
& x<0.100, \\
& 500.100-x \approx 0.100 \\
& \frac{x^{2}}{0.100}=5.56 \times 10^{-10}
\end{aligned}
$$

$x=7.45 \times 10^{-6} \mathrm{~m}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$p H=-\log _{10}\left(7.45 \times 10^{-6}\right)$ $p H=5.13$

For comparison, $\mathrm{pH}=1.00$ for a strong acid like HCl $\mathrm{pH}=2.17$ for 0.10 M nitrous acid $\mathrm{pH}=7.00$ for distilled water
$0.100 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, Find PH

$$
\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \rightarrow \mathrm{Na}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}
$$

$N_{a}{ }^{+}$: Neutral: Na+ has no H+ to donate, and its positive charge makes accepting a proton unlikely.

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}: \quad \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-}
$$

LI WEAK ACID, so we think acetate ion can hang on to an H+ and be a BASE.

We need to solve ACETATE ION's equilibrium:

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-} ; \mathrm{Kb}=\frac{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}
$$ the Ka for its conjugate (acetic acid) on page A-13. We can convert.

$$
\begin{aligned}
K a \times k b= & 1.0 \times 10^{-14} \\
\left(1.7 \times 10^{-5}\right) & k b \\
& =1.0 \times 10^{-14} \\
K b & =5.89 \times 10^{-10}
\end{aligned}
$$

158

$$
\begin{aligned}
& \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}_{;}^{-} \mathrm{K}=\frac{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]} \\
& \text {Set up an equilibrium chart! }
\end{aligned}
$$

| Species | [Initial] | $\Delta$ | $[$ Equilibrium] |
| :---: | :---: | :---: | :---: |
| $0 H^{-}$ | 0 | $+X$ | $X$ |
| $\mathrm{H}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | 0 | $+X$ | $X$ |
| $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ | 0.100 | $-X$ | $0.100-x$ |

$$
h b=5.89 \times 10^{-10}
$$

Let "x" equal the change in hydroxide ion concentration.

$$
\begin{aligned}
& \frac{x^{2}}{0.100-x}=5.89 \times 10^{-10} \\
& \downarrow x<60.100,500.100-x=0.100 \\
& \frac{x^{2}}{0.100}=5.89 \times 10^{-10} \\
& x=7.67 \times 10^{-6} \mathrm{~m}=\left[\mathrm{OH}^{-}\right]
\end{aligned}
$$

$$
\begin{aligned}
\text { POL } & =5.11 \\
\text { PH } & =14.00-5.11 \\
& =8.89
\end{aligned}
$$

For comparison:
0.100 M sodium acetate, $\mathrm{pH}=8.89$
0.100 M ammonia, $\mathrm{pH}=11.13$
0.100 M NaOH (strong base), $\mathrm{pH}=13.00$

The acetate ion is basic, but it's a very weak base!

