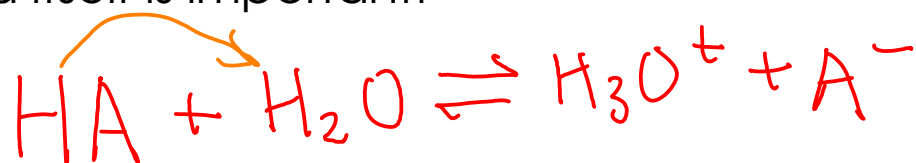


For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!



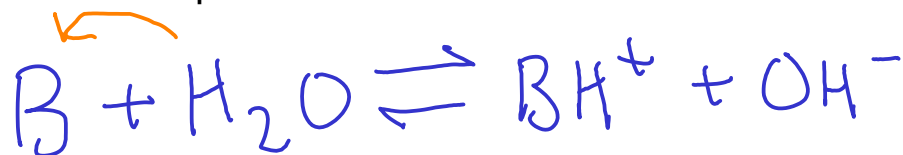
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

acid ionization constant

Again, water's concentration will not change significantly, so it is folded into the ionization constant

(HA) = concentration of undissociated acid

For a WEAK BASE, equilibrium does not lie far to the right. The ionization equilibrium of the base itself is important!



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

base ionization constant

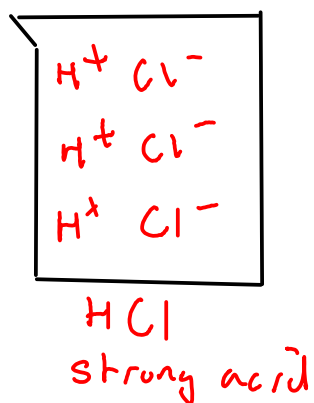
Values for K_a and K_b can often be found in data books / tables / or on the web.

In Ebbing, this data is in the appendices, on pages A-13 and A-14

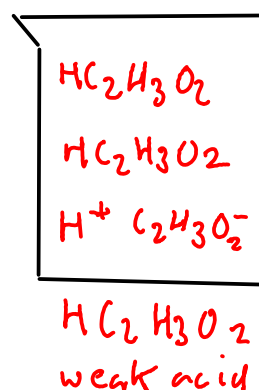
WEAK ELECTROLYTES

- In solutions of weak acids or bases, the UNDISSOCIATED form is present in significantly high concentration.

- The pH of a solution of weak acid will be HIGHER than the pH of a strong acid solution with the same nominal concentration!



VS



Fewer molecules of the weak acid ionize, so the concentration of hydrogen/hydronium ion is lower, meaning a higher pH!

- The pH of a solution of weak base will be LOWER than the pH of a strong base solution with the same nominal concentration!

Consider a 0.100M solution of nitrous acid, a WEAK ACID (HNO_2)



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

Found on page A-14 in Ebbing 10th edition. These K values are determined experimentally like other equilibrium constants.

What is the pH of the solution?

Set up an equilibrium chart as we did in chapter 14, and we'll use it to figure out hydronium concentration, since that relates to pH...

Species	[Initial]	Δ	[Equilibrium]
H_3O^+	0	+X	X
NO_2^-	0	+X	X
HNO_2	0.100	-X	0.100 - X

Define "x" as the change in hydronium ion concentration...

$$\frac{(x)(x)}{(0.100 - x)} = 4.5 \times 10^{-4}$$

Similar to expressions we got in the chapter 14 equilibrium problems! We'll need to solve for "x" ...

$$\frac{(x)(x)}{(0.100-x)} = 4.5 \times 10^{-4}$$

$$\frac{x^2}{0.100-x} = 4.5 \times 10^{-4}$$

Assume $x \ll 0.100$, then
 $0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 4.5 \times 10^{-4}$$

$$x = 0.0067082039 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = 2.17$$

This is a quadratic, We can solve it with the quadratic equation:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

When is it safe to assume that "x" is small relative to the starting concentration?
 When the value of K is a factor of 1000x or more smaller than the starting concentration!

Solving the quadratic gives a pH of 2.19 ...

Compare:

- Weak acid 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 M HNO_3 , what is pH?



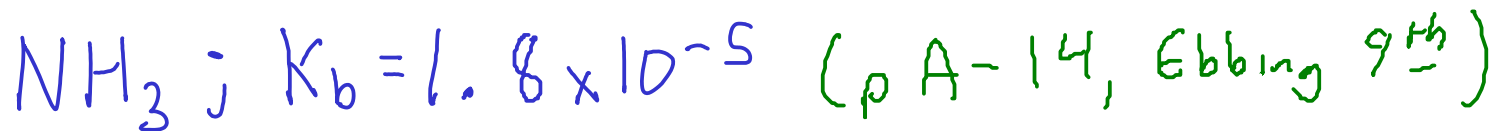
$$[\text{H}_3\text{O}^+] = [\text{HNO}_3]_{\text{nominal}} = 0.10 \text{ M}$$

$$\text{pH} = 1.00$$

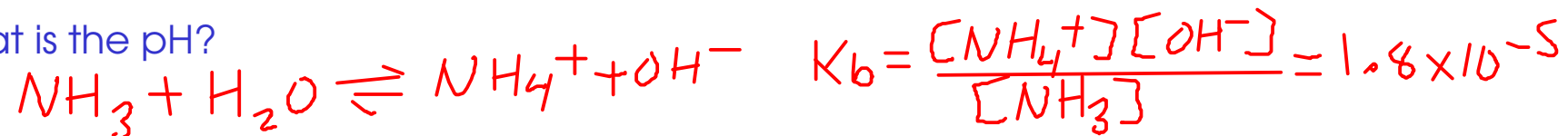
The stronger the acid:

- 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:



What is the pH?



We need to solve for HYDROXIDE concentration, since we can relate that to the pH!

Species	[Initial]	Δ	[Equilibrium]
NH_4^+	0	+X	X
OH^-	0	+X	X
NH_3	0.100	-X	0.100 - X

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

$$\frac{(x)(x)}{(0.100 - x)} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

Solve by quadratic, or simplify...

$$\downarrow 0.100 - x \approx 0.100, x \ll 0.100$$

$$\frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$$x = 0.0013416408 \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log_{10} [\text{OH}^-] = 2.87$$

$$\text{pH} + \text{pOH} = 14.00, \text{ so}$$

$$\text{pH} = 14.00 - 2.87 = \boxed{11.13}$$

Caution! We solved for HYDROXIDE concentration, so you've got to convert to hydronium before you get a final answer. Convert either before or after taking the negative log!

If you'd solved the quadratic equation instead of using the simplifying assumption $x \ll 0.100$, you would have gotten a pH of 11.13 (same as our answer here!)

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$$\text{pH}_{\text{NH}_3} \approx 11.13$$



$$[\text{OH}^-] = [\text{NaOH}]_{\text{nominal}} = 0.100 \text{ M}$$

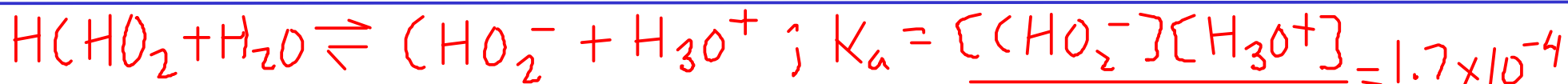
$$\text{pOH} = 1.00$$

$$\text{pH} = 13.00$$

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)

Find the pH and the degree of ionization for an 0.10 M solution of formic acid: HCHO_2



Let's find pH first ... We'll need to solve for the concentration of hydronium ion...

$[\text{HCHO}_2]$

(value from p A-14 in textbook...)

Species	[Initial]	Δ	[Equilibrium]
CHO_2^-	0	+X	X
H_3O^+	0	+X	X
HCHO_2	0.10	-X	0.10 - X

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

$$\frac{(x)(x)}{0.10 - x} = 1.7 \times 10^{-4}$$

$$\frac{x^2}{0.10 - x} = 1.7 \times 10^{-4}$$

$x \ll 0.10$

$\downarrow 0.10 - x \approx 0.10$

$$\frac{x^2}{0.10} = 1.7 \times 10^{-4}$$

$$x = 0.0041231056 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$\text{pH} = 2.38$$

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

$$\text{DOI} = \frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]_{\text{nominal}}} = \frac{[\text{H}_3\text{O}^+]}{[\text{HCHO}_2]_{\text{nominal}}}$$

$$= \frac{0.0041231056}{0.10} = \boxed{0.041}$$

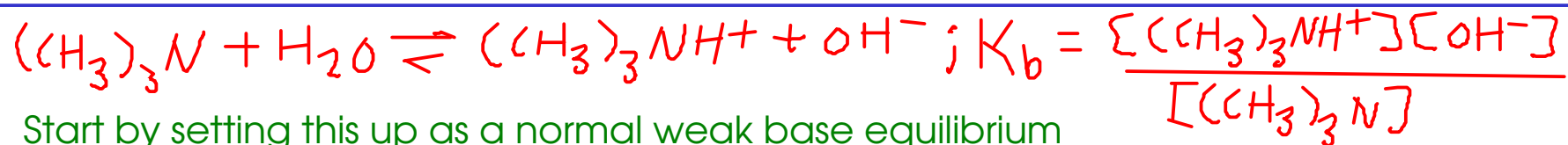
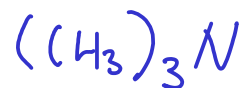
... often, DOI will be expressed as a percentage ... called percent ionization.

$$\% \text{ionization} = \text{DOI} \times 100 = 4.1\%$$

So, the 0.1 M solution of formic acid is 4.1% ionized.

When you do Experiment 16A. By Le Chateleur'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.

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



Start by setting this up as a normal weak base equilibrium problem!

Species	[Initial]	Δ	[Equilibrium]
$(\text{CH}_3)_3\text{NH}^+$	0	+X	X
OH^-	0	+X	X
$(\text{CH}_3)_3\text{N}$	0.25	-X	0.25 - X

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

$$\frac{(x)(x)}{0.25 - x} = K_b$$

$$\frac{x^2}{0.25 - x} = K_b$$

If we want to find K_b , we need to find the value of "x" somehow.

Since we know the pH is 11.63, we'll find the pOH ($\text{pH} + \text{pOH} = 14.00$), and then we'll find the (OH^-) (and "x"!) from the pOH...

$$\frac{x^2}{0.25-x} = K_b, \quad \text{pH} = 11.63$$

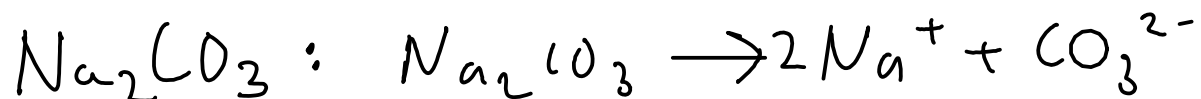
$$\text{pH} + \text{pOH} = 14.00, \quad \text{pOH} = 14.00 - 11.63 = 2.37$$

$$[\text{OH}^-] = 10^{-2.37} = 0.0042657952 = x$$

$$\text{So, } K_b = \frac{(0.0042657952)^2}{0.25 - 0.0042657952} = 7.4 \times 10^{-5} = K_b$$

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



Do any of these ions have acidic or basic properties?

Na^+ : neutral. Not a proton donor or a proton acceptor

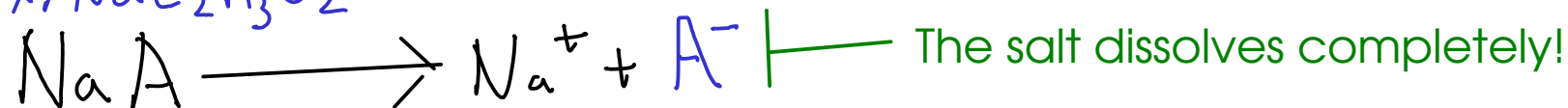
CO_3^{2-} : BASIC, since it can accept protons to form the weak acid CARBONIC ACID in solution.



ACID

BASE

SALT OF A WEAK ACID

ex: $\text{NaC}_2\text{H}_3\text{O}_2$ 

For this reaction to occur, HA MUST be stable in water. In other words, a weak acid.



The anion is a BASE. It can accept a proton from water to form the weak (therefore stable as a molecule!) acid HA

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad \left| \text{--- This is the base ionization constant for } \text{A}^- \right.$$

Since A^- and HA are a conjugate pair, the ionization constants are related!

$$K_w = (K_{a,\text{HA}})(K_{b,\text{A}^-})$$

1.0×10^{-14}

$$14 = \text{p}K_a + \text{p}K_b$$

You will generally not find both the K_a AND K_b for a conjugate pair in the literature, since one can be easily converted to the other!