Consider a 0.100M solution of nitrous acid, a WEAK ACID $\left(HNO_2\right)$

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 4.5 \times 10^{-4}$$

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?

To find pH, we need to solve the equilibrium above for the hydronium ion concentration.

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

Let 'x' equal the change in concetration of hydronium ion

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

This looks familiar. Very similar to the equilbrium problems we worked in Chapter 14

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

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

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

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

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

Assume: $x << 0.100$, so $0.100 - x \approx 0.100$

Since Ka is small, there will be only a small amount of acid that ionizes. That means 'x', which represents the change in the molarity of the nitrous acid (as well as the hydronium ion) should be small relative to 0.1 ... making 0.1-x essnetially equal to 0.1 ...

When is it safe to assume that x it small enough to drop from the subtraction term? When the initial acid/base concentration is about 1000+ times greater than the equilibrium constant.

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

$$x^2 = 4.5 \times 10^{-5}$$

$$x = 0.0067082039 = [H_3O^+]$$

$$pH = 2.17$$

(Solving the original quadratic equation 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 stopn acid like nitric acid:
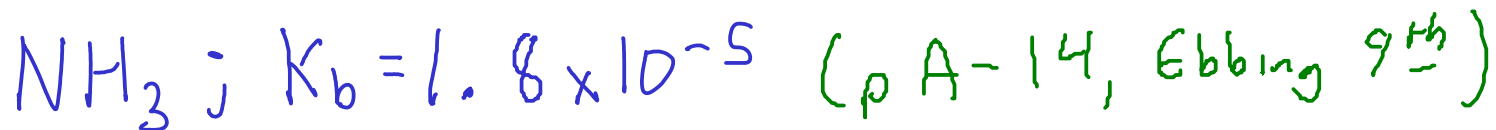
$$0.10 \text{ m } HNO_3, \text{ what is pH?}$$

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

$$0.10 M HNO_3, \quad [H_3O^+] = 0.10 M$$

$$pH = 1.00$$

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)

Consider an 0.100 M solution of the weak base ammonia:

$$NH_3 ; K_b = 1.8 \times 10^{-5} \quad (pA-14, \text{ Ebbing } 9^{th})$$

What is the pH?

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

We need to solve this equilibrium, but which term will help us find pH?

We'll solve for the HYDROXIDE concentration since it can be easily related to 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 hydroxide ion concentration

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

154

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

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

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

$$x^2 = 1.8 \times 10^{-6}$$

$$x = 0.0013416408 = [OH^-]$$

$$pOH = -\log_{10}(0.0013416408) = 2.87$$

Since pH + pOH = 14.00, ...

$$pH = 14 - 2.87$$

$$\boxed{pH = 11.13}$$

(If you'd solved the original quadratic equation, you would have gotten a pH of 11.13 ... same as we got here to two significant figures)

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

$pH_{1\,NH_3} = 11.13$

$NaOH \rightarrow Na^+ + OH^-$

So, 0.100 M NaOH has $[OH^-] = 0.100$

$pOH = -\log_{10}(.100) = 1.00$

$pH = 14.00 - 1.00 = \boxed{13.00}$

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: $HCHO_2$

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.7 \times 10^{-4}$$

Value from page A-13 in Ebbing...

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

Let 'x' equal the change in hydronium ion concentration

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

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

Assume $x \ll 0.10$
$0.10 - x \approx 0.10$

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

$$x^2 = 1.7 \times 10^{-5}$$

$$x = 0.0041231056 = [H_3O^+]$$

$$\boxed{pH = 2.38}$$

What is DEGREE OF IONIZATION? It's the fraction of a weak acid or base that ionizes in water!

$$\frac{[CHO_2^-]}{[HCHO_2]_{initial}} = \frac{[H_3O^+]}{[HCHO_2]_{initial}} = \frac{0.0041231056}{0.10} = \boxed{0.041 = DOI}$$

Sometimes we express this as a percent to make it clearer ... this is called PERCENT IONIZATION:

$$\% = DOI \times 100\% = \boxed{4.1\% \text{ Ionized}}$$

If we DILUTED THE ACID, ...

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

... amount of water goes up, equilibrium shifts to RIGHT.

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.

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

$$(CH_3)_3N$$
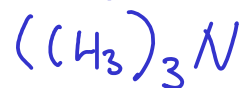
$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \text{???}$$

How do we find Kb? First, let's set this up like a "normal" equilibrium problem:

Species	[Initial]	Δ	[Equilibrium]
$(CH_3)NH^+$	0	$+x$	x
OH^-	0	$+x$	x
$(CH_3)_3N$	0.25	$-x$	$0.25-x$

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

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

If we want to find the value of Kb, then we have to find some other way to find out the value of 'x' ...

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

We know that 'x' equals the HYDROXIDE ION concentration. We don't know this value at the moment, but we do know pH ... which gives us HYDRONIUM ION ooncentration.

$pH = 11.63$, so $10^{-11.63} = [H_3O^+]$

$[H_3O^+] = 2.34422822 \times 10^{-12}$

Using the water equilibrium ... $[H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$(2.34422822 \times 10^{-12})[OH^-] = 1.00 \times 10^{-14}$

$[OH^-] = 0.004265795 2 = x$

Plug 'x' into the experssion at the top of this page to find Kb ...

$$K_b = \frac{x^2}{0.25 - x} = \frac{(0.004265795 2)^2}{0.25 - 0.004265795 2}$$

$$\boxed{K_b = 7.4 \times 10^{-5}}$$

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 <u>WEAK ACIDS</u> tend to form <u>BASIC</u> solutions

- Salts made from <u>WEAK BASES</u> tend to form <u>ACIDIC</u> solutions

$$Na_2CO_3: \quad Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$
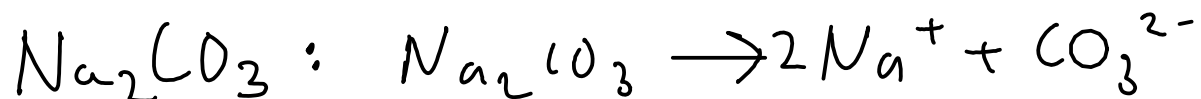
Do any of these ions have acidic or basic properties?

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.

$$H_2CO_3 + 2H_2O \rightleftharpoons 2H_3O^+ + CO_3^{-2}$$

ACID   BASE

SALT OF A WEAK ACID

ex: $NaC_2H_3O_2$

$$NaA \longrightarrow Na^+ + A^-$$ ← The salt dissolves completely!

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

$$A^- + H_2O \rightleftharpoons HA + OH^-$$ ← ... but the ionization of the salt's anion is an EQUILIBRIUM!

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

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$ ← This is the base ionization constant for $\bar{A}$

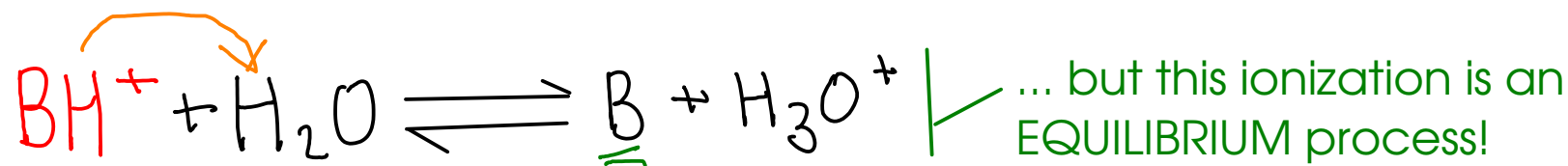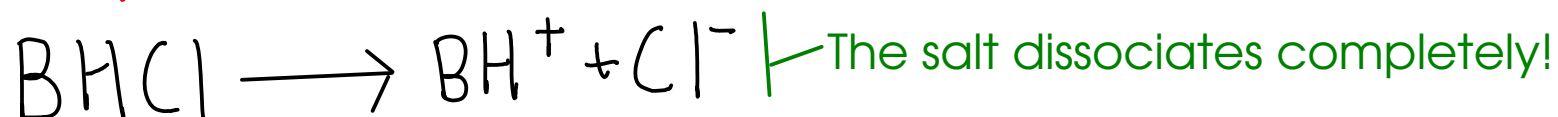Since $\bar{A}$ and HA are a conjugate pair, the ionization constants are related!

You will generally not find both the Ka AND Kb for a conjugate pair in the literature, since one can be easily converted to the other!
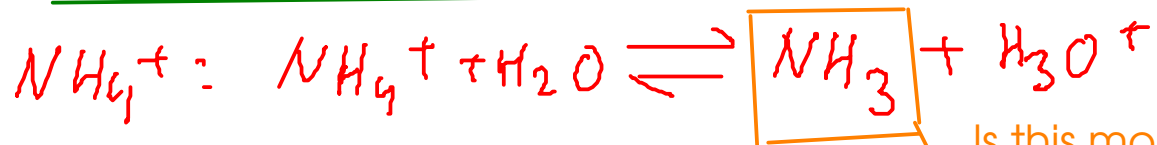
$$K_w = (K_{a,HA})(K_{b,A^-})$$

1.0×10^{-14}

$$14 \approx pK_a + pK_b$$

SALT OF A WEAK BASE

ex: NH_4Cl

$$BHCl \longrightarrow BH^+ + Cl^-$$ The salt dissociates completely!

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$ ... but this ionization is an EQUILIBRIUM process!

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$ Acid ionization constant for BH^+

$$K_w = \left(K_{a,BH^+}\right)\left(K_{b,B}\right)$$
1.0×10^{-14}

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!

$0.100 \text{ M } NH_4Cl \ldots$ Find the pH of the solution

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$ <-- is the salt acidic, basic, or neutral?

$NH_4^+: NH_4^+ + H_2O \rightleftharpoons \boxed{NH_3} + H_3O^+$

Is this molecule stable in water? YES.
Ammonia is a common weak base that
can exist in water.

$Cl^-: Cl^- + H_2O \rightleftharpoons \boxed{HCl} + OH^-$
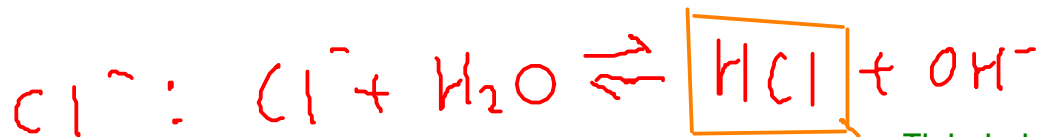
This is hydrochloric acid ... a STRONG ACID.
HCl completely ionizes in water, meaning
that HCl is NOT stable in water. Therefore,
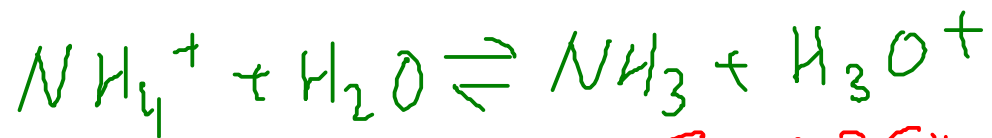Cl- is NEUTRAL.

So, we solve the equilibrium of the AMMONIUM ION:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
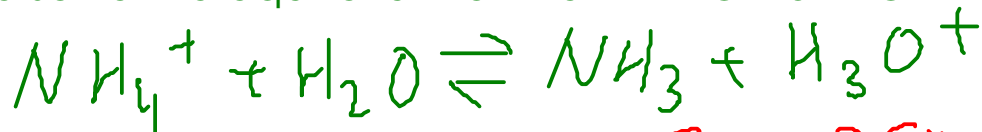
$$K_{a, NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = ?$$

On pages A-13, there's no Ka for ammonium ion ... but there IS a Kb on A-14 for ammonia:

$$K_{b, NH_3} = 1.8 \times 10^{-5} \quad ; \quad (K_{a, NH_4^+})(K_{b, NH_3}) = 1.0 \times 10^{-14}$$

$$(K_{a, NH_4^+})(1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$$

$$K_{a, NH_4^+} = 5.56 \times 10^{-10}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$K_{a, NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.56 \times 10^{-10}$$

Now solve this equilibrium just like you would for any weak acid ...

Species	[Initial]	Δ	[Equilibrium]
NH_3	0	$+X$	X
H_3O^+	0	$+X$	X
NH_4^+	0.100	$-X$	$0.100 - X$

$$\frac{(x)(x)}{0.100 - x} = 5.56 \times 10^{-10}$$

$$\frac{x^2}{0.100 - x} = 5.56 \times 10^{-10}$$

$$\downarrow x \ll 0.100$$

$$\frac{x^2}{0.100} = 5.56 \times 10^{-10}$$

$$x^2 = 5.56 \times 10^{-11}$$

$$x = 7.45 \times 10^{-6} = [H_3O^+]$$

$$\boxed{pH = 5.13}$$

Compare:
pH - 1.00 for 0.10 M strong acid
pH = 2.17 for 0.10 M nitrous acid (weak acid)
pH = 7.00 for distilled water.