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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

acid
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!

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

base
ionization
constant

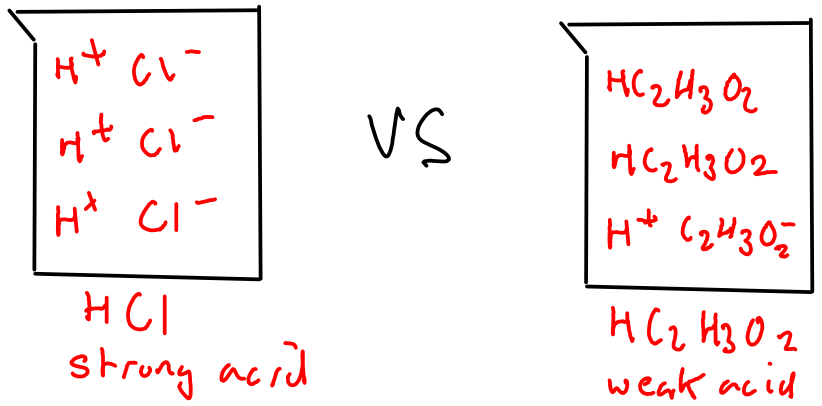
Values for Ka and Kb can often be found in data books / tables / or on the web.

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!



Fewer molecules of the weak acid ionize, so the concnetration 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)

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

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

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

What is the pH of the solution?

To find pH, we need to determine the concentration of hydronium ion at equilibrium, but this time we can't assume all the acid ionizes. So we need to solve the equilibrium expression for the hydronium ion concentration.

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

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

This looks familiar. It's very similar to the equilibrium problems we solved in Chapter 14.

$$\frac{(x)(x)}{(0.100-x)} = 4.5\times10^{-4}$$

$$\frac{x^2}{0.100-x} = 4.5\times10^{-4}$$

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

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

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

Ka is small, so 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) should be small relative to 0.1. IF 'x' is small relative to 0.1, then ...

$$0.100-x \approx 0.100$$

When is it safe to assume x is small enough to drop from one of the terms? When the initial acid or base concentration is about 1000x larger than the value of Ka (Ka/(HA) >=1000)

$$\frac{x^2}{0.100} = 4.5\times10^{-4}$$

$$x^2 = 4.5\times10^{-5}$$

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

$$\boxed{\text{So pH} = 2.17}$$

(Solving the full 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 m HNO_3, what is pH?

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

0.10 m HNO_3, $[H_3O^+] = 0.10$

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 ; $K_b = 1.8 \times 10^{-5}$ (p A-14, Ebbing 9th)

What is the pH?

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

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

We need to solve this to fnd equilibrium concentations, but which one will give us pH?

We want to solve fot the HYDROXIDE concentration, since it's closely related to - and can be easily converted to - pH.

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

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

$$1.8 \times 10^{-5} = \frac{x^2}{0{,}100 - x}$$

This is a QUADRATIC EQUATION, but we can simplify it if 'x' is small compared to 0.100 ...

$x << 0{,}100$, so $0{,}100 - x \approx 0{,}100$

$$1{,}8 \times 10^{-5} = \frac{x^2}{0{,}100}$$

$$1{,}8 \times 10^{-6} = x^2$$

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

Be careful hjere! We have calculated HYDROXIDE concentration, not HYDRONIUM ... so we can't just take the negative logarithm of this and say we're done!

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

Since $pH + pOH = 14.00$*,

$$\boxed{pH = 11.13}$$

*If you'd solved using the quadratic equation, you would have gotten a pH of 11.13 ... same as we got here.

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

$pH_{NH_3} = 11.13$

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

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: $HCHO_2$

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

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

Constant's value at 25C came from Ebbing page A-13 (10th edition)

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

$$\frac{(x)(x)}{0.1 - x} = 1.7 \times 10^{-4}$$

$$\frac{x^2}{0.1 - x} = 1.7 \times 10^{-4}$$

If we assume 'x' is small compared to 0.10, then ... $0.10 - x \approx 0.10$

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

$$x = 0.004123105 6$$

$x = 0.0041231056 = [H_3O^+]$

So $\boxed{pH = 2.38}$

... But what is DEGREE OF IONIZATION? DEGREE OF IONIZATION is the fraction of a weak acid or base that ionizes in water.

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

Sometimes, we express this in terms of PERCENT IONIZATION because we're more comfortable thinking about percents:

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

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 percenjt) 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?

$(CH_3)_3N$

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

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

How do we find Kb? First, let's set this up like a normal equilibrium calculation.

Species	[Initial]	Δ	[Equilibrium]
$(CH_3)_3NH^+$	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, we have to find some independent way of finding 'x'!

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

We know the pH ... which gives us the HYDRONIUM ION concentration. We can calculate the HYDROXIDE concentration (and the value of 'x') using the hydronium concentration.

$$pH = 11.63 \; ; \; pH + pOH = 14.00$$

$$pOH = 2.37$$

$$[OH^-] = 10^{-2.37} = 0.004265795 2$$

Since 'x' = (OH-) (see the chart we made on the last page ...

$$x = 0.0042657952$$

Now all we have to do is to plug 'x' back into the equilibrium expression...

$$K_b = \frac{x^2}{0.25 - x} = \frac{(0.0042657952)^2}{0.25 - 0.0042657952}$$

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

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 WEAK ACIDS tend to form BASIC solutions

- Salts made from WEAK BASES tend to form ACIDIC solutions

Na_2CO_3 : $Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

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 $\overset{-}{A}$

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

$$\underset{1.0\times10^{-14}}{K_w} = (K_{a,HA})(K_{b,A^-})$$

$$14 = pK_a + pK_b$$

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!

SALT OF A WEAK BASE

ex: NH_4Cl

$$BHCl \longrightarrow BH^+ + Cl^-$$

The salt dissociates completely!

$$BH^+ + H_2O \rightleftharpoons \underline{B} + H_3O^+$$

... but this ionization is an EQUILIBRIUM process!

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

Acid ionization constant for BH^+

$$\underset{1.0\times10^{-14}}{K_w} = (K_{a,BH^+})(K_{b,B})$$

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!