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

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

$$\underbrace{K_a}_{\text{acid ionization constant}} = \frac{[H_3O^+][A^-]}{\underbrace{[HA]}_{\text{(HA) = concentration of undissociated acid}}}$$

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

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

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

$$\underbrace{K_b}_{\text{base ionization constant}} = \frac{[BH^+][OH^-]}{[B]}$$

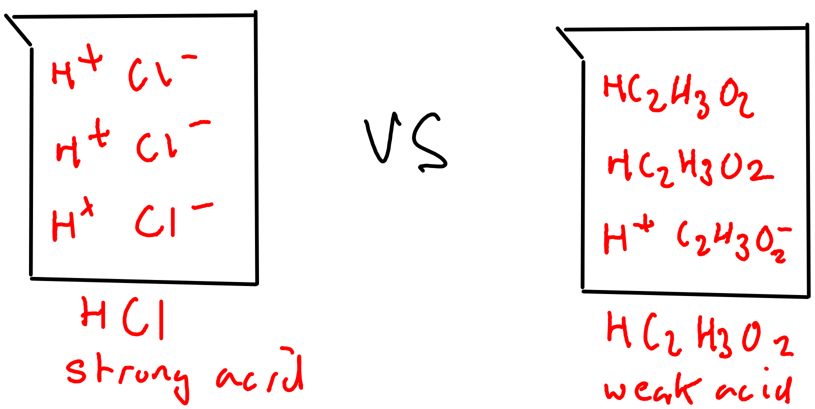
Values for Ka and Kb can often be found in data books / tables / or on the web.

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?

Set up a chart and solve an equilibrium problem, since this time we CANNOT ignore the equilibrium of the acid - not all nitrous acid molecules make hydronium!

| Species | [Initial] | $\Delta$ | [Equilibrium] |
|---|---|---|---|
| $H_3O^+$ | 0 | $+x$ | $x$ |
| $NO_2^-$ | 0 | $+x$ | $x$ |
| $HNO_2$ | 0.100 | $-x$ | $0.100-x$ |

Let "x" equal the increase in hydronium ion concentraiton.

Plug equilibrium values into Ka expression...

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

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

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

Assume x << 0.100, so
0.100 -x = .100

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

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

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

$$\boxed{pH \simeq 2.17}$$

(Solving the quadratic gives a pH of 2.19)

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 is safe to assume the value of "x" is small relative to the initial concentration? When the equilibrium constant is at least 1000x smaller than the initial concentration is. If that's not true, you should solve the quadratic!

# 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?

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

0.10 M $HNO_3$, $[H_3O^+] = 0.10$ 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:

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

What is the pH?

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

| Species | [Initial] | $\Delta$ | [Equilibrium] |
|---|---|---|---|
| $NH_4^+$ | 0 | +X | X |
| $OH^-$ | 0 | +X | X |
| $NH_3$ | 0.100 | −X | 0.100−X |

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

To get pH, we need to first find the concentration of HYDROXIDE (it's directly relatable to hydronium and pH...)

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

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

Assume x << 0.100, so
0.100-x = 0.100

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

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

$$pOH = 2.87$$

$$\boxed{pH = 11.13}$$

$pOH = -\log[OH^-]$

$pH + pOH = 14.00$

(Solving this with the quadratic equation gives a pH of 11.13)

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, $[OH^-] = 0.100$

$pOH = -\log_{10}(0.100) = 1.00$

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

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: $HCHO_2$

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

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.7\times10^{-4}$$

Ka from page A-13 in E&G textbook...

Start off by calculating pH ...

| 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 increase in hydronium ion concentration...

$$\frac{(x)(x)}{(0.10-x)} = 1.7\times10^{-4}$$

$$\frac{x^2}{0.10-x} = 1.7\times10^{-4}$$

Assume x <<0.10, so
0.10-x = 0.10

$$\frac{x^2}{0.10} = 1.7\times10^{-4}$$

$$x = 0.004123105 6 = [H_3O^+]$$

$$pH = 2.38$$

On the next page, we'll find the degree of ionization...