Introducing Acids and Bases

Recall: $H^+ + H_2O <\text{-------}> H_3O^+$ **hydronium ion**

in aqueous solution---level of H_3O^+ proportional to H^+, so we can either use $[H^+]$ or $[H_3O^+]$ to represent acidity of solution!

autoprotolysis of water: $2 H_2O <\text{-----}> H_3O^+ + OH^-$
   or : $H_2O <\text{------}> H^+ + OH^-$ $\qquad$ $K_w = [H^+][OH^-] = 1 \times 10^{-14}$
$\hspace{10cm}$ at 25° C

Bronsted and Lowery Defn:
   Acid---proton donor $\qquad\qquad$ $HA + B <\text{-----}> BH^+A^-$ (salt)
   Base---proton acid

$HA <\text{--------}> H^+ + A^-$ $\qquad$ A^- is **conjugate base** of HA

$RNH_2 + H^+ <\text{--------}> RNH_3^+$ $\quad$ RNH_3^+ is **conjugate acid** of RNH_2

$$\underset{\substack{\text{Acetic acid} \\ \text{Acid}}}{CH_3-\overset{\displaystyle \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}{\underset{\displaystyle \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H}{C}}} \quad + \quad \underset{\substack{\text{Methylamine} \\ \text{Base}}}{CH_3-\overset{\cdot\cdot}{\underset{\displaystyle H}{N}}\cdots H} \quad \rightleftharpoons \quad \underset{\substack{\text{Acetate ion} \\ \text{Base}}}{CH_3-\overset{\displaystyle \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}{\underset{\displaystyle \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}^-}{C}}} \quad + \quad \underset{\substack{\text{Methylammonium ion} \\ \text{Acid}}}{CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\overset{+}{\cdots} H}$$

Conjugate pair

Conjugate pair
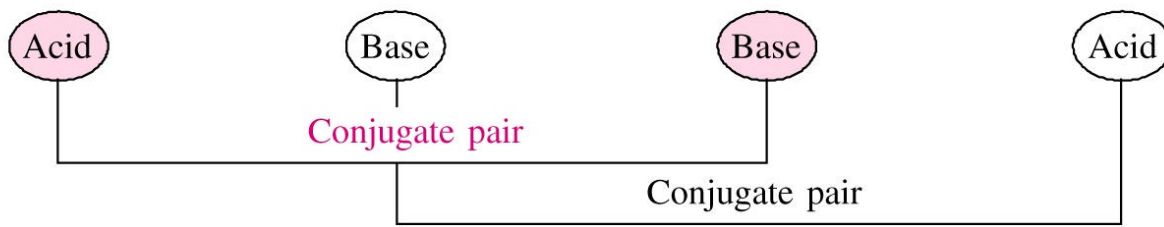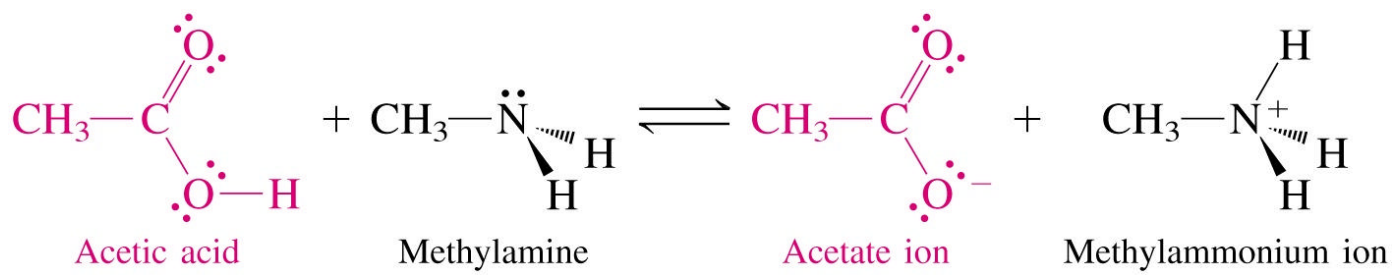
Consequences of Autoprotolysis rxn of Water:

•can always find concentration of H^+ or OH^- if other species is known since in an aqueous solution---the autoprotolysis rxn is always in equilibrium!----**product of $[H^+]$ $[OH^-]$ must equal 1×10^{-14}**

e.g.---if you know $[H^+] = 2 \times 10^{-3}$ M; **then $[OH^-] = K_w / [H^+] = 5 \times 10^{-12}$**

•in pure water---$[H^+]$ $[OH^-] = x^2 = 10^{-14}$; **Hence $[H^+] = [OH^-] = 1 \times 10^{-7}$**
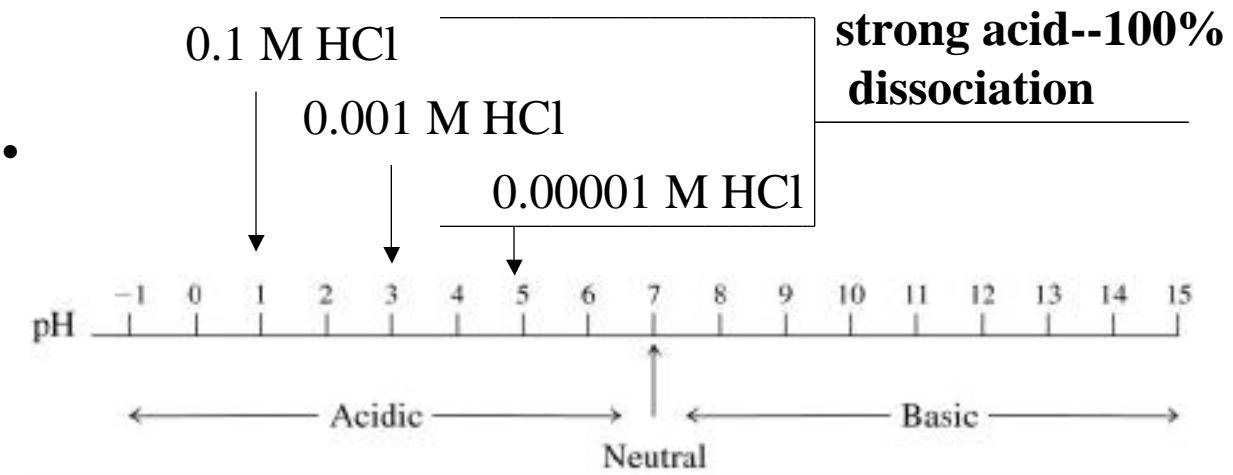
pH and $[H^{\pm}]$;

define pH $= -$ log $[H^+]$ (we will see later that pH $= -$log $a_H{}^+$ ---but in dilute solutions---$[H^+] = a_H{}^+$)

if $[H^+] - 3.8 \times 10^{-8}$; pH $= -$ log$(3.8 \times 10^{-8}) = 7.42$

pH Scale

pH = -log [H$^+$] ; therefore: [H$^+$] = 10^{-pH}

(can have pH values < 0 (negative #) and > 14--very strong acids/bases at very high concentrations)

0.1 M HCl   **strong acid--100%**
                                             dissociation
0.001 M HCl

0.00001 M HCl

pH   -1 0   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15

←———— Acidic ————→ ←———— Basic ————→
Neutral

- What about 1x10^{-8} M HCl?   pH=8   ??
  - A dilute acid cannot be basic.   **We shall see--in a minute!**

Baking soda

Lake Ontario

Human urine

Saliva, pH 5.7–7.1

Tomato juice

Average pH of rainfall, Toronto, February 1979

Apples

Lemon juice

Acidic

Alkaline

Lye

Ammonia

Milk of magnesia

Seawater

Human blood

Neutral

Milk

Theoretical "pure" rain, pH 5.6

Most fish species die, pH 4.5–5.0

Vinegar

Most acidic rainfall recorded in U.S. at Wheeling, W. Va.

Battery acid
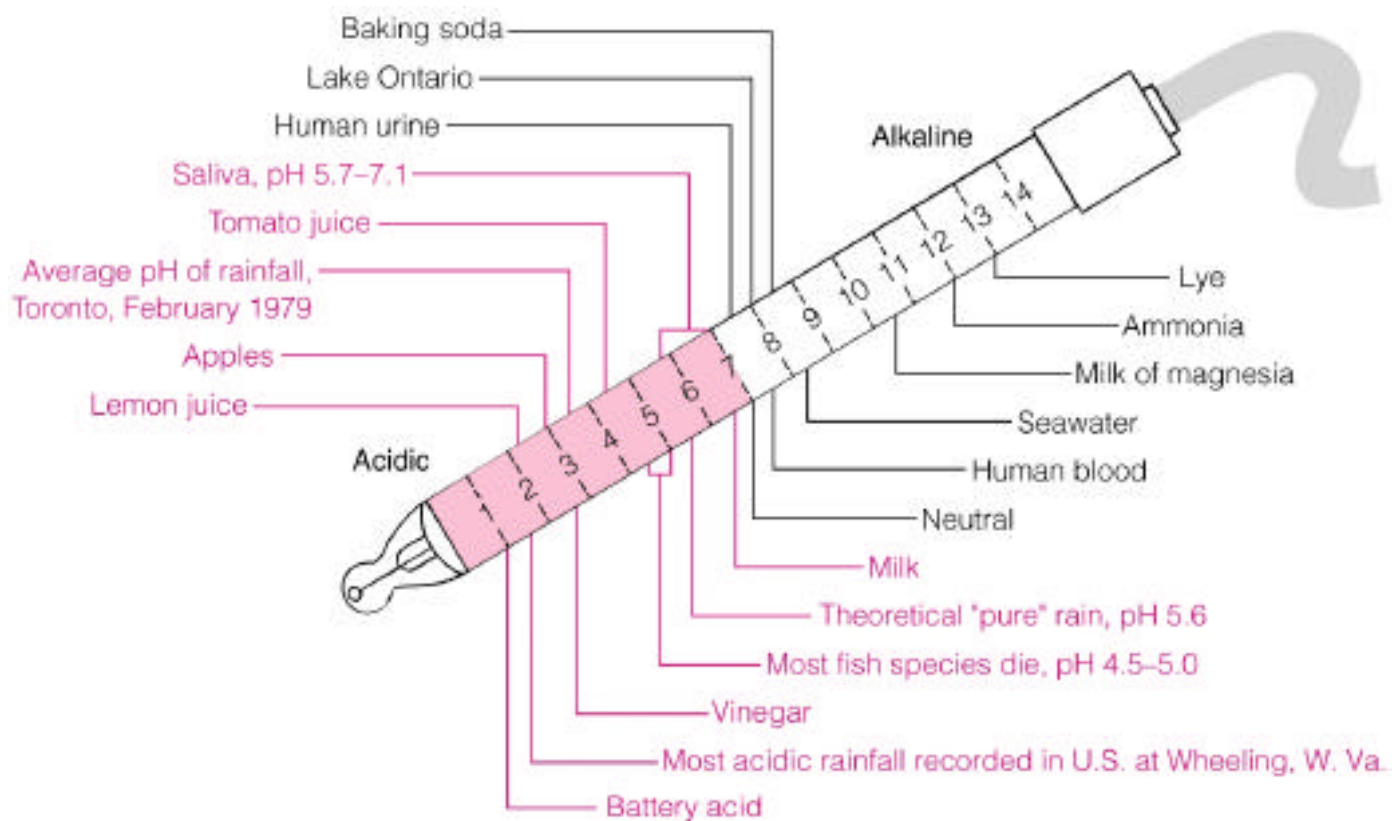
pH for strong acid and strong base determined by moles of H^+ or OH^- generated by complete dissociation of these species;
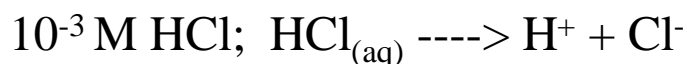
10^{-3} M HCl; $HCl_{(aq)}$ ----> H^+ + Cl^-
  (arrow in only one direction due to fact that equilibrium is
   achieved only when products are present)

pH = -log $[10^{-3}]$ = 3.00   (report pH to two decimals--usually)

What is pH of 4.2 x 10^{-3} M $HClO_4$?   pH = -log (4.2 x 10^{-3}) = 2.38

What is pH of 4.2 x 10^{-3} M NaOH? in this case need to use
  K_w expression---and assume all $[OH^-]$ in water soln is coming from
   exogenous base:
$$[H^+] = K_w/[OH^-] = 10^{-14} / 4.2 \text{ x } 10^{-3} = 2.3_8 \text{ x } 10^{-12}$$

    therefore pH = -log (2.3$_8$ x 10^{-12}) = 11.62

Water Auto-dissociation
the "leveling effect"

For strong acids or bases---can neglect [H$^+$] and [OH$^-$] arising from autoprotolysis of water----when concentrations of acids and bases are $> 10^{-6}$ M----however as you use more dilute concentrations--- the contribution of H$^+$ and OH$^-$ are dictrated by water equilibrium reaction!
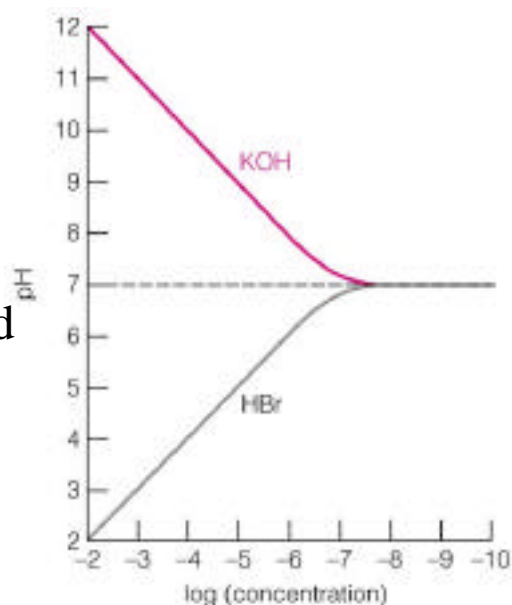
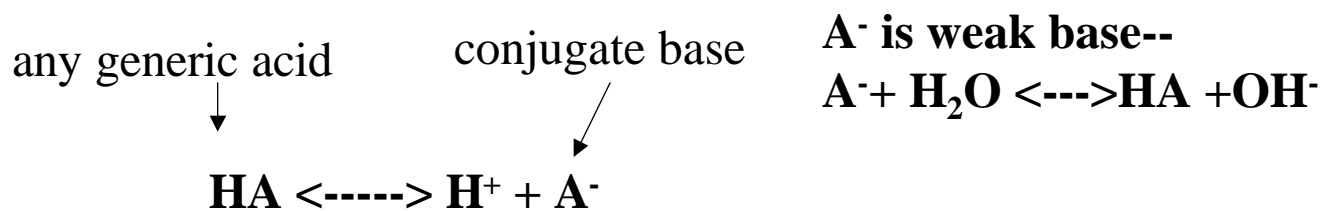pH of 10^{-10} M HNO$_3$ = ? = pH 7.00

pH of 10^{-8} M HCl = ?

$[H^+]_{tot} = [H^+]_{HCl} + [H^+]_{H20} = 10^{-8} + 10^{-7}$

$= 1.1 \times 10^{-7}$; pH = -log 1.1×10^{-7} = 6.96

The pH of a very dilute acid can never go above pH=7.0
    or the pH of the very dilute base can not go below pH=7.0

Weak Acid Dissociation Constants

any generic acid

conjugate base

A⁻ is weak base--
A⁻+ H₂O <--->HA +OH⁻

HA <-----> H⁺ + A⁻

in water, formally--should be written as: HA + H₂O <---> H₃O⁺ + A⁻
but we can neglect the water in writing any equilibrium constant

$$K_a = \frac{[H^+][A^-]}{[HA]} = \text{acid dissociation constant}$$

For diprotic acids: H₂A <-----> H⁺ + HA⁻ <-----> H⁺ + A⁻²

(Diprotic acid = two removable protons)

$$K_{a(1)} = \frac{[H^+][HA^-]}{[H_2A]} = \text{first acid dissociation constant}$$

$$K_{a(2)} = \frac{[H^+][A^{-2}]}{[HA^-]} = \text{second acid dissociation constant}$$
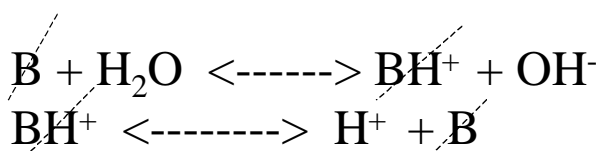
Weak Bases:

B + H$_2$O <-------> BH$^+$ + OH$^-$

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

K_b values are small for weak bases!
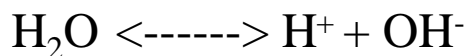
BH$^+$ is conjugate acid of B; a salt of BH$^+$Cl$^-$ dissolved in water would likely yield an acidic pH solution!---

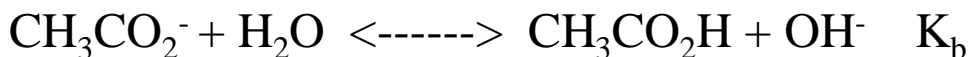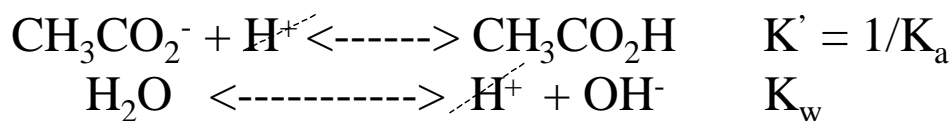Relationship between K_a and K_b of weak acids/bases conjugate pairs:

B + H$_2$O <------> BH$^+$ + OH$^-$ K$_b$

BH$^+$ <--------> H$^+$ + B   K$_a$
_____

H$_2$O <------> H$^+$ + OH$^-$ K$_w$

Thus (recall from manipulation of K values:

K$_w$ = K$_a$ K$_b$
and   K$_a$ = K$_w$/ K$_b$

Another example---**What is K_b of acetate---the conjugate base of acetic acid?**

$$CH_3CO_2H \longleftrightarrow CH_3CO_2^- + H^+ \quad K_a$$

can write reverse reaction as:

$$CH_3CO_2^- + H^+ \longleftrightarrow CH_3CO_2H \quad K' = 1/K_a$$
$$H_2O \longleftrightarrow H^+ + OH^- \quad K_w$$

$$CH_3CO_2^- + H_2O \longleftrightarrow CH_3CO_2H + OH^- \quad K_b$$

therefore: $K_b = K_w(1/K_a) = K_w / K_a$

for acetic acid---$K_a = 1.75 \times 10^{-5}$; therefore K_b for acetate =
$$10^{-14}/ (1.75 \times 10^{-5}) = \mathbf{5.7 \times 10^{-10}}$$

What is K_a for methylammonium ion ($CH_3NH_3^+$)?

if $K_b = 4.4 \times 10^{-4}$ (amine); $K_a = 1 \times 10^{-14} / 4.4 \times 10^{-4} = \mathbf{2.3 \times 10^{-11}}$

pK$_a$ and pK$_b$:

$$pK_a = -\log K_a \qquad \text{and} \qquad pK_b = -\log K_b$$

Therefore---the stronger the acid---the lower/smaller its pK$_a$
the stronger the base---the lower/smaller its pK$_b$
or---the greater the pK$_a$ of the conjugate acid

Phosphate

Hydroxyl

HO⁻P

HO

Ammonium ⟶ H

N+   CH$_3$

pyridoxal phosphate

pK$_a$	Group	K$_a$
1.40	POH$_{(1)}$	0.04
3.44	OH	3.6×10^{-4}
6.01	POH$_{(2)}$	9.8×10^{-7}
8.45	NH	3.5×10^{-9}

Comparing Acid/Base Strength

- More convenient to write log(K) values
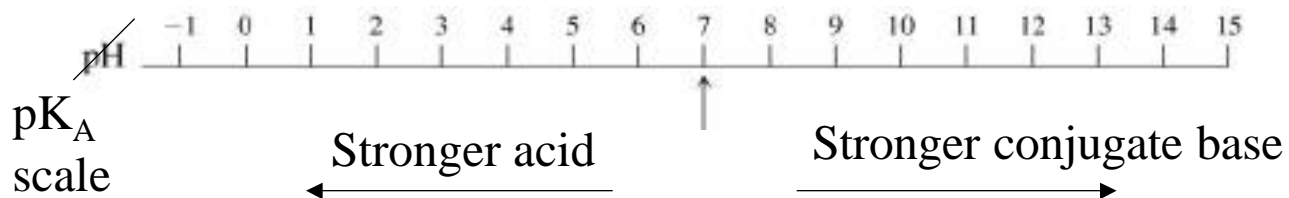- Less zeros to write

$$pK_A = -\log K_A$$

$$pK_B = -\log K_B$$

Acetic acid $pK_A = 4.75$

Chloroacetic acid $pK_A = 2.87$

Aminoacetic acid $pK_A = 2.35$

Complete table in Appendix B

pH scale: −1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

pK_A scale

Stronger acid

Stronger conjugate base

Calculating pH for Weak Acid Dissociation

- First step, assume $[A^-] \sim [H^+]$

HA <-----> H$^+$ + A$^-$

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

$[A^-]=[H^+]=x$
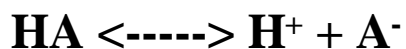
$F=[HA]+[A^-]$

F = total concentration of A species---formal conc

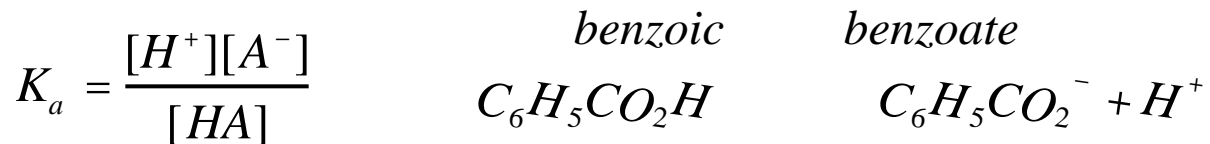|	[HA]	[H$^+$]	[A$^-$]
initial	F	0	0
final	F-x	x	x

- This ignores the small [H$^+$] ($<10^{-7}$ M) from the dissociation of water

$$K_a = \frac{x^2}{F - x}$$

Example--Weak Acid Problem

- What is the pH of a 0.02 M solution of benzoic acid?

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

$[H^+]=x$; $[A^-]=x$

$F=[HA]+[A^-]=0.02$ M

	benzoic $C_6H_5CO_2H$	*benzoate* $C_6H_5CO_2^-$	$+H^+$
t=0	F	0	0
t=eq	F-x	x	x

- Lookup pK_A from table (appendix B): $pK_A = 4.20$

$$K_a = \frac{x^2}{F-x} \qquad 6.28 \times 10^{-5} = \frac{x^2}{0.02-x}$$

Solve for x: $\qquad 0 = x^2 + 6.28 \times 10^{-5} x - \left(6.28 \times 10^{-5} \; 0.02\right)$

Two approaches can be used to solve-----can get rid of quadratic by using successive approximation approach:

- Just in case the programmable calculator is out of reach
- 6.28×10^{-5} is a small number
- What if we neglect the $-bx$ term

$$K_a = \frac{x^2}{F-x}$$

$$0 = x^2 + 6.28 \times 10^{-5} x - \left(6.28 \times 10^{-5} \; 0.02\right)$$

1) approximation:
   (F-x) ~ F
   True if F>>x

$$x^2 = \left(6.28 \times 10^{-5} \; 0.02\right)$$

$$x = \sqrt{6.28 \times 10^{-5} \; 0.02}$$

drop

$$\left[H^+\right] = \sqrt{K_A \; F_{HA}}$$

$$x \quad \sqrt{6.28 \times 10^{-5} \; 0.02}$$

$$x \quad 1.12 \times 10^{-3} M = \left[H^+\right]$$

- Now check assumptions

Checking/Refining the Approximation

- Assumption $F \gg x$ $C_6H_5CO_2H \qquad\qquad C_6H_5CO_2^- + H^+$

$$pK_a = 4.20$$

$$K_a = \frac{x^2}{F - x} \qquad\qquad F = 0.02M$$

1st approximation : $x_1 = [H^+] = 1.12 \times 10^{-3}$

- Now check the approximation--plug back in for x in F-x term---and then solve for x^2 and then x as the square root!

$$x^2 = 6.28 \times 10^{-5} \ (0.02 - x)$$

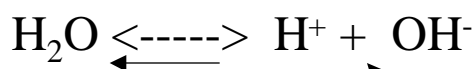$$x^2 \quad 6.28 \times 10^{-5} \ (0.02 - 1.12 \times 10^{-3})$$

$$x \quad 1.09 \times 10^{-3} \quad \longleftarrow \quad \text{slightly less than initial answer!}$$

- Keep plugging x_i, back into the equation until x_i is constant

But what about [H$^+$] from dissociation of water? Do we have too worry about this?

- Water also dissociates to give [H$^+$] and [OH-]

$$H_2O \longleftrightarrow H^+ + OH^-$$

$[OH^-] = K_w / [H^+]$

$$\left[OH^-\right] = \frac{10^{-14}}{1.09 \times 10^{-3}} = 9.17 \times 10^{-12}$$

$C_6H_5CO_2H \qquad C_6H_5CO_2^- + H^+$

$$pK_A = 4.20$$

$$x \quad 1.09 \times 10^{-3} = [H^+]$$

- Water dissociation gives --[H$^+$]$_{H2O}$ = [OH$^-$]$_{H2O}$
- Final pH of solution is = -log [H$^+$]$_{total}$
- [H$^+$]$_{total}$ = [H$^+$]$_{H2O}$ + [H$^+$]$_{HA}$
- [H$^+$]$_{total}$ = 9.17x10^{-12} + 1.09 x 10^{-3} = 1.09x10^{-3} M

why so small--? --autoprotolysis rxn shifted to left---due to H$^+$ from HA reaction!

Second approach to solve such problems---use formula for solution of quadratic equation!

$$0 = x^2 + 6.28 \times 10^{-5} x - \left(6.28 \times 10^{-5} \ 0.02 \right)$$

$0 = x^2 + 6.28 \times 10^{-5} x - 1.25_6 \times 10^{-6}$

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

$a = 1$
$b = 6.28 \times 10^{-5}$
$c = 1.25_6 \times 10^{-6}$

<u>two solutions---</u>

1.09 x 10⁻³

- 1.09 x 10⁻³ ⟵   **reject---[H⁺] cannot be negative!**

- Fraction of dissociation

$$\frac{\text{ionic form of acid}}{\text{total acid forms}} = \frac{[A^-]}{[A^-] + [HA]} = \text{fraction dissociated}$$
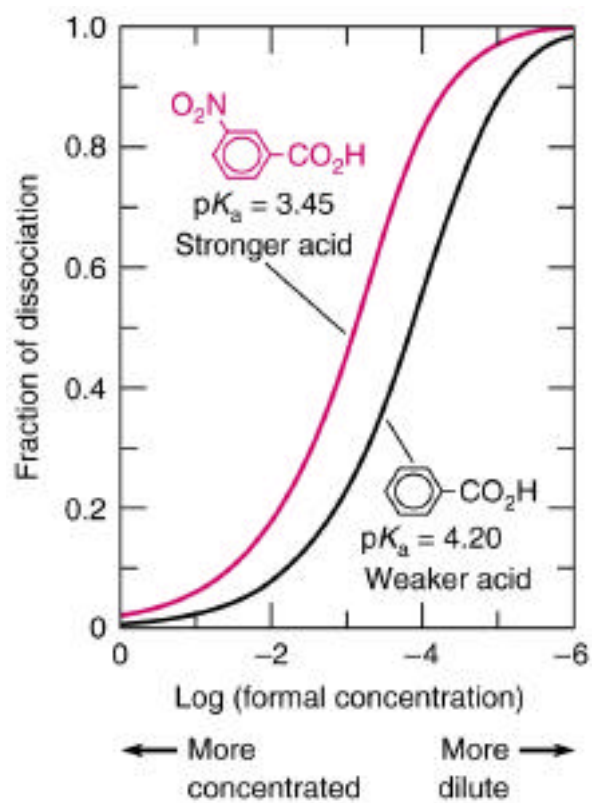
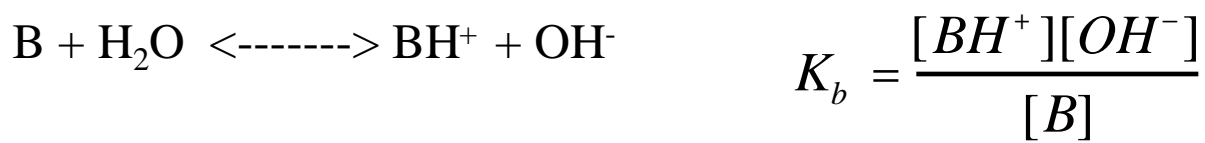$[A^-] = 1.09 \times 10^{-3}$ ← From our last example

$F = 0.02\ M = [HA] + [A^-]$

$$\%D = \text{fraction x } 100 = \frac{1.09 \times 10^{-3}}{0.02} = 5.4\%$$

- This is one way to define a weak acid (or base) from a strong one
- A strong acid (or base) is nearly 100% dissociated in dilute solution

at same concentration---fraction of dissociation for stronger acid is greater!!

For weak base-- similar treatment to find pH of solution

$B + H_2O$ <-------> $BH^+ + OH^-$ $K_b = \dfrac{[BH^+][OH^-]}{[B]}$
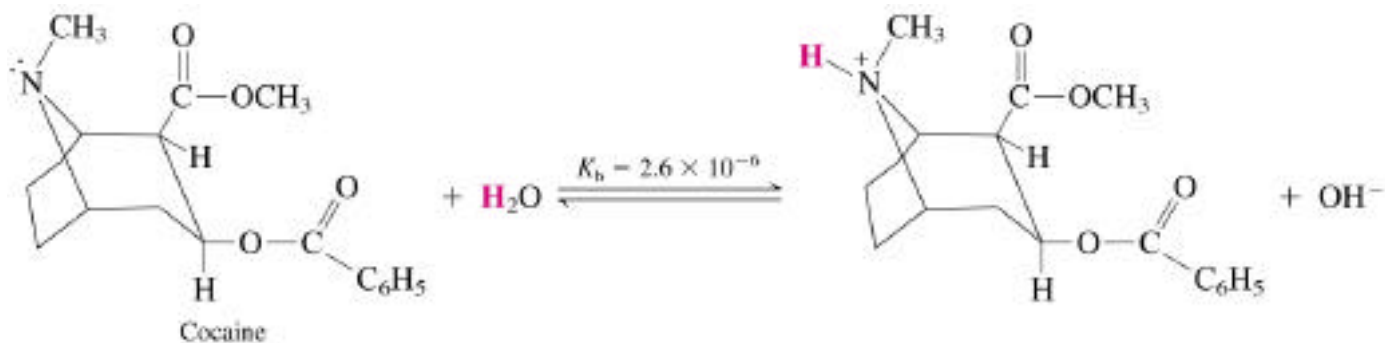
again--nearly all the OH⁻ in soln comes from the base reaction---not the autoprotolysis of water!

$F = [B] + [BH^+]$; $[B] = F - [BH^+] = F - x$

$K_b = \dfrac{x^2}{F - x}$ this time, x = [OH⁻]

however----now when you find x by either successive approx. or solution of quadratic equation, to find pH you must remember:

$[H^+] = K_w / [OH^-]$

Cocaine

What is pH of 0.0372 M solution of cocaine?

$$\frac{x^2}{0.0372 - x} = 2.6\text{x}10^{-6} = K_b$$

by method of successive approx; $x^2 = 9.67_2 \text{ x } 10^{-8}$

$x = 3.11 \text{ x } 10^{-4}$

plug back into denominator in K_b expression:

$x^2 / (0.0372 - 3.11 \text{ x } 10^{-4}) = 2.6 \text{ x } 10^{-6}$

$x^2 / 0.0369 = 2.6 \text{ x } 10^{-6}$; $x = 3.09_7 \text{ x } 10^{-4} = 3.10 \text{ x } 10^{-4} = [OH^-]$

therefore--- $[H^+] = K_w / [OH^-] = 10^{-14} / 3.10 \times 10^{-4} = 3.2_2 \times 10^{-11}$

$$\textbf{pH} = \textbf{-log } \textbf{(3.2}_2 \textbf{ x 10}^{-11}\textbf{)} = \textbf{10.49}$$

fraction reacted?

fraction = $[BH^+] / ([B] + [BH^+])$; but $[BH^+] = [OH^-]$

therefore--- fraction $= 3.10 \times 10^{-4} / 0.0372 = 0.0083$

or 0.83 % is reacted with water!

F -total conc. of base initially present!

What is pH of solution of 0.05 M sodium benzoate?

This is a salt---that yields 100% dissociation yielding Na^+ and benzoate ions at equal concentration in solution!

but we know that benzoic acid is the protonated form of benzoate anion----it has K_a of 6.28×10^{-5} ;

thus K_b of benzoate--the conjugate base of benzoic acid :
$K_b = K_w / K_a = 10^{-14} / 6.28 \times 10^{-5} = 1.5_9 \times 10^{-10}$

$$K_b = \frac{x^2}{0.05 - x} = 1.5_9 \times 10^{-10}$$

solve for x- ([OH⁻])--by successive approx-- = 2.8 x 10⁻⁶ M

$[H^+] = K_w / [OH^-] = 10^{-14} / 2.8 \times 10^{-6} = 3.5 \times 10^{-9}$;
pH = -log (3.5×10^{-9}) = 8.45