There are three definitions for acids and bases we will need to understand.

Arrhenius Concept: an acid supplies H^+ to an aqueous solution. A base supplies OH^- to an aqueous solution. This is the oldest definition but most limiting.

Bronsted-Lowry Concept: an acid is a proton (H^+) donor. A base is a proton (H^+) acceptor. When an acid donates a proton, it becomes a base (acting in the reverse direction); when a base accepts a proton, it becomes an acid (acting in the reverse direction). You will need to identify conjugate acid-base pairs.

Example: Formic acid, HCOOH: (IUPAC name: methanoic acid)

$$HCOOH + H_2O = H_3O^+ + HCOO^-$$

$$H\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}H + H_2O = H_3O^+ + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^-$$

A_1 B_2 A_2 B_1

Mar 10-8:30 AM

Lewis Concept: an acid is an electron pair acceptor. A base is an electron pair donor. This is the most wide-ranging of the three (i.e. it works for everything). Examples of Lewis acids include Al^{3+}, H^+, BF_3. Examples of Lewis bases include NO_2^-, NH_3, and H_2O.

Identify the Lewis acid and base in each of the following reactions and name to product ion that forms:

$Cu^{2+}(aq) + 4\ddot{N}H_3(aq) = Cu(NH_3)_4^{2+}(aq)$ ← tetramine copper (II)

LA LB

$I^-(aq) + I_2(aq) = I_3^-(aq)$

LB LA

$Fe^{3+}(aq) + 6H_2\ddot{O}(l) = Fe(H_2O)_6^{3+}(aq)$ hexaaqua iron (III)

LA LB

Indicate the B-L acid-base conjugate pairs and identify the Lewis acid and base in the hydrated (III) iron(II) ion, $[Fe(H_2O)_6]^{3+}$

$$[Fe(H_2O)_6]^{3+} + H_2O = H_3O^+ + [Fe(H_2O)_5OH]^{+2}$$

A_1 B_2 A_2 B_1

Mar 10-8:31 AM

Acid-Base Strength

The strength of an acid is indicated by the equilibrium position of the dissociation reaction. If the equilibrium lies far to the left (as indicated by the small value of K_a), the acid does not dissociate to any great extent and is weak:

$$HA = H^+ + A^-$$

	HA	H^+	A^-
i	1000	0	0
c	-20	+20	+20
e	980	20	20

If the equilibrium lies far to the right, the acid strongly dissociates and is strong:

$$HA = H^+ + A^-$$

	HA	H^+	A^-
i	1000	0	0
c	-999	+999	+999
e	1	999	999

Note that: the stronger the acid, the weaker its conjugate base (B-L acids)
the stronger the base, the weaker its conjugate acid (B-L bases)

You need to memorize the strong acids and bases given below. All others can be considered weak.

Mar 10-8:31 AM

Strong acids

HCl	hydrochloric acid	$HClO_3$	chloric acid
HBr	hydrobromic acid	$HClO_4$	perchloric acid
HI	hydroiodic acid	H_2SO_4	sulfuric acid
HNO_3	nitric acid		

Mar 10-8:32 AM

Strong Bases

Metal Hydroxides: these are group 1 and group 2 metals bonded to a hydroxyl group. For example NaOH, $Mg(OH)_2$, etc.

Metal Oxides: these are group 1 and group 2 metals bonded with oxygen. In water they "attack" the water molecule and break it up to form hydroxide ion, OH^-.

$$K_2O + H_2O = 2K^+ + 2OH^-$$

Mar 10-8:32 AM

Acid-Base Behavior and Chemical Structure

Sometimes you will need to compare the strengths of acids. This can be done by considering the structure of the acids. Two general trends are useful in explaining differences:

For acid hydrides (HCl, HBr, etc.) the acidity increases within a group as the size of the central atom increases. This is because bond strength decreases as size increases. HF is a weak acid because the H-F bond is strong. Another factor to consider is the ability of the anion formed (X^-) – the greater the stability of the conjugate base, the stronger the acid is. For example,

$HI > HBr > HCl$

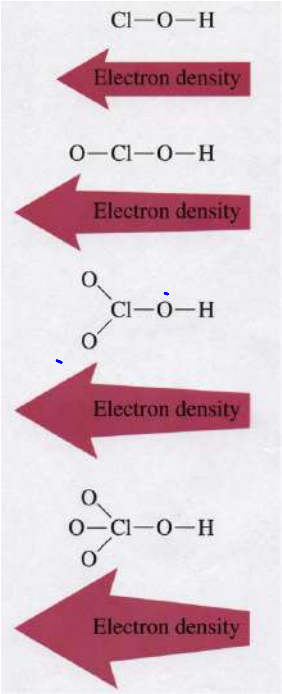
For oxyacids that have the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom. For example,

$HClO > HBrO > HIO$

$HClO_3$ is stronger than $HBrO_3$

Mar 10-8:32 AM

3. For oxyacids that have the a central atom, acid strength increases as the number of oxygen atoms attached to the central atom increases.



For example, H_2SO_4 is stronger than H_2SO_3

Mar 10-8:32 AM

Acid-Base Properties of Oxides

An acidic oxide is a nonmetal oxide. Nonmetal oxides (also referred to as **acid anhydrides**) react in water to produce acidic solutions. For example,

$$NO_2(g) + H_2O(l) = HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

A basic oxide is a metal oxide. Metal oxides (also referred to as **basic anhydrides**) react with water to produce a basic solution. For example,

$$Na_2O(s) + H_2O(l) = 2NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

Mar 10-8:33 AM

Autoionization of Water

$H_2O_{(l)} + H_2O_{(l)} = H_3O^+_{(aq)} + OH^-_{(aq)}$

Water is an **amphoteric** substance (it can act as a B-L acid or base). For the autoionization reaction,

$2\ H_2O(l)\ =\ H_3O^+(aq)\ +\ OH^-(aq)$ and $K_w = 1.0 \times 10^{-14}$ at 25°C

$K_w = [H_3O^+][OH^-]$

$\quad\quad\ \ x \quad\quad x$

$1 \cdot 10^{-14} = x^2$

$x = 1 \cdot 10^{-7}\ M$

(the simplified reaction can be expressed as: $H_2O(l)\ =\ H^+(aq)\ +\ OH^-(aq)$
but H^+ immediately attacks a water to form H_3O^+)

Note: H^+ and H_3O^+ are used interchangeably

$HOH = H^+_{(aq)} + OH^-_{(aq)}$

$H_2O + H_2O = H_3O^+ + OH^-$

If Add acid, $[H_3O^+]\uparrow$, $\leftarrow$ $[OH^-]\downarrow$

10^{-4} . . . . . . 10^{-10}

CRITICAL POINT: in aqueous solutions, the ion product $[H_3O^+][OH^-]$ always must equal 1.0×10^{-14} at 25°C.

To "p" something in chemistry means to take the negative log base 10. So,

$pH = -\log[H^+]$ or $-\log[H_3O^+]$ psoup = -log[soup]

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

pH Scale

$[H^+]$	1	10^{-7}	10^{-14}
pH	0	7	14

acid $\longleftarrow$ base $\longrightarrow$

Again note: $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$

$pK_w = pH + pOH$

$pH + pOH = 14$

Also note: $pX = -\log[X]$

$[X] = 10^{-px}$

Problem: Fill in

pH = 6.88

pOH = 7.12

$[H^+] =$ $10^{-6.88} = 1.32 \cdot 10^{-7}$ M

$[OH^-] =$ $10^{-7.12} = 7.59 \cdot 10^{-8}$ M

acidic, basic, or neutral?

Mar 10-8:33 AM

Calculating the pH of Acidic Solutions

In order to properly assess acid-base problems in aqueous solution, you must

recognize that autoionization of water is ALWAYS occurring in aqueous solutions, and

be able to determine whether autoionization will contribute significantly to the acid-base character of a solution.

Strong Acid Solutions

Calculating the pH of strong acid solutions is in general fairly straightforward, because the dissociation equilibrium lies so far to the right - that is, the acid completely dissociates. The autoionization of water is negligible as a contributor of H^+ to the solution (via Le Chatelier). The rare exception to this is when your concentrated acid is exceptionally dilute ($< 10^{-6}$ M). In that case water can contribute a relatively large proportion of H^+ to the solution.

The bottom line is the $[H^+]$ at equilibrium = $[\text{strong acid}]_o$, except in very dilute solutions.

Problem: Calculate the pH and $[OH^-]$ of a 5.0×10^{-3} M perchloric acid solution. Indicate Bronsted-Lowry acid-base conjugate pairs.

$$\underset{A_1}{HClO_4} + \underset{B_2}{H_2O} = \underset{A_2}{H_3O^+} + \underset{B_1}{ClO_4^-}$$

I $5.0 \cdot 10^{-3}$ 0 0

C $-5.0 \cdot 10^{-3} \xrightarrow{100\%}$ $+5.0 \cdot 10^{-3}$ $+5.0 \cdot 10^{-3}$

E

$[H_3O^+] = 5.0 \cdot 10^{-3}$ $pH = -\log(5.0 \cdot 10^{-3})$

$= 2.30$

$[H_3O^+][OH^-] = 1 \cdot 10^{-14}$

$$[OH^-] = \frac{1 \cdot 10^{-14}}{5.0 \cdot 10^{-3}} = 2.0 \cdot 10^{-12} \text{ M}$$

Mar 10-8:33 AM

Weak Acid Solutions

Weak acids do not dissociate completely in aqueous solution. They are somewhat stable molecules with covalent character - not completely ionic like strong acids (or in the special case of HF, so strongly ionic that water can't "pull it apart").

Solving weak acid problems is just like solving equilibrium problems with small K's we have done before. For weak acids, keep in mind the following key points:

although there are often several reactions that can produce H^+, **usually only one predominates**. You can make the proper judgment based on the values of the equilibrium constants for the reactions.

you must test any assumptions that you make regarding the extent of dissociation of a weak acid (i.e. $[HA] = [HA]_o$).

Mar 10-8:34 AM

Determining pH and Percent Dissociation

Problem: Calculate the pH of a 0.500 M aqueous solution of formic (methanoic) acid. The $K_a = 1.77 \times 10^{-4}$. Determine the percent dissociation of the acid in solution.

$$\begin{array}{lcccccc} & HCOOH & + & H_2O & = & H_3O^+ & + & HCOO^- \\ I & .500 & & & & 0 & & 0 \\ C & -x & & & & +x & & +x \\ E & .500-x & & & & x & & x \end{array}$$

$$1.77 \cdot 10^{-4} = \frac{x^2}{.500-x} \qquad x = 9.32 \cdot 10^{-3}$$

$$\therefore \ pH = -\log 9.32 \cdot 10^{-3} = \underline{2.031}$$

$$\% \text{ Ionization} = \frac{x}{\text{original}} \cdot 100 = \frac{9.32 \cdot 10^{-3}}{.500} \times 100 = \underline{1.86\%}$$

Mar 10-8:34 AM

For a given weak acid, the percent dissociation increases as the acid becomes more dilute.

Problem: Calculate the percent dissociation of acetic acid (K_a = 1.8 X 10^{-5}) in each of the following solutions:

a) 1.00 M

	$HC_2H_3O_2 + H_2O =$	$H_3O^+ +$	$C_2H_3O_2^-$
I	1.00	0	0
C	$-x$	$+x$	$+x$
E	$1.00-x$	x	x

$$1.8 \cdot 10^{-5} = \frac{x^2}{1.00-x} \qquad x = 4.23 \cdot 10^{-3}\ M = [H_3O^+]$$

$$\% \text{ diss} = \frac{4.23 \cdot 10^{-3}}{1.00} \times 100 = .423\%$$

b) 0.10 M

Now,

$$1.8 \cdot 10^{-5} = \frac{x^2}{.100-x} \qquad x = 1.33 \cdot 10^{-3}\ M$$

$$\% \text{ diss} = \frac{1.33 \cdot 10^{-3}}{.100} \times 100$$

1.33%

Mar 10-8:34 AM

The pH of a Mixture of Weak Acids

With regard to calculating the pH of a mixture of weak acids, the basic question remains: **Which is the dominant equilibrium** among the several that are followed? If you can resolve that, then the problem reduces to the pH of what is effectively one species in solution.

Problem: Calculate the pH of a mixture of 2.00 M formic acid (K_a = 1.77 X 10^{-4}), and 1.50 M hypobromous acid (K_a = 2.06 X 10^{-9}). What is the concentration of both hypobromite ion and hydroxide ion at equilibrium? Calculate the percent dissociation of the formic acid.

1st: formic acid dominates, $10^{-4} \gg 10^{-9}$

$$HCOOH + H_2O = H_3O^+ + HCOO^-$$

$2.00 - x$ $\qquad x \qquad x$

$$1.77 \cdot 10^{-4} = \frac{x^2}{2.00-x} \qquad x = 1.87 \cdot 10^{-2}\ M$$

Next:

	$HBrO + H_2O =$	$H_3O^+ +$	BrO^-
I	1.50	$1.87 \cdot 10^{-2}$	0
C	$-x$	$+x$	$+x$
E	$1.50-x$	$1.87 \cdot 10^{-2} + x$	x

$$2.06 \cdot 10^{-9} = \frac{(1.87 \cdot 10^{-2} + x)(x)}{(1.50 - x)}$$

$$x = 1.65 \cdot 10^{-7}\ M$$

$$[H_3O^+] = 1.87 \cdot 10^{-2} + 1.65 \cdot 10^{-7} = 1.87 \cdot 10^{-2}$$

$$pH = -\log(1.87 \cdot 10^{-2}) = \underline{1.73}$$

$$[OBr^-] = 1.65 \cdot 10^{-7}\ M$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \cdot 10^{-14}}{1.87 \cdot 10^{-2}} = 5.33 \cdot 10^{-13}\ M$$

$$\% \text{ diss} = \frac{1.87 \cdot 10^{-2}}{2.00} \times 100 = .935\%$$

Mar 10-8:34 AM

K_a From Percent Dissociation

Problem: In a 0.500 M solution, uric acid ($HC_5H_3N_4O_4$) is 1.6% dissociated. Calculate the K_a value for uric acid.

$.500 \times .016 = .00800\,M$

$HC_5H_3N_4O_4 + H_2O \rightleftharpoons H_3O^+ + C_5H_3N_4O_4^-$

$.500 - .00800 \qquad .0080 \qquad .0080$

$$K_A = \frac{(.0080)^2}{.500 - .00800} = 1.30 \cdot 10^{-4}$$

Mar 10-8:35 AM

Polyprotic Acids

A polyprotic acid can furnish more than one proton to a solution. Note that in every case $K_{a1} >>> K_{a2}$. Why do you think this is so? This means that for most polyprotic acids, the first dissociation is the one that dominates and we can neglect the second and third dissociations. Hence, pH problems involving polyprotic acids reduce to finding the pH from the dominant equation.

Problem: Calculate the pH of a 0.100 M H_2SO_4 solution. Note that $K_{a2} = 1.2 \times 10^{-2}$

1st ionization:

$H_2SO_4 + H_2O \xrightarrow{100\%} H_3O^+ + HSO_4^-$

$.100 \qquad .100 \qquad .100$

2nd ionization

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

I: $.100 \qquad .100 \qquad 0$

C: $-x \qquad +x \qquad +x$

E: $.100 - x \qquad .100 + x \qquad x$

$$1.2 \cdot 10^{-2} = \frac{(.100 + x)(x)}{(.100 - x)} \qquad x = .00985\,M$$

$[H_3O^+] = .100 + .00985 = .110\,M$

$pH = -\log(.110) = \underline{.959}$

$$[OH^-] = \frac{1 \cdot 10^{-14}}{.110} =$$

Mar 10-8:35 AM

Problem:

Calculate the pH of a 1.40 M oxalic acid solution and the equilibrium concentrations of $H_2C_2O_4$, $HC_2O_4^-$, $C_2O_4^{2-}$, and OH^-. Note: $K_{a1} = 6.5 X 10^{-2}$, $K_{a2} = 6.1 X 10^{-5}$.

1st ionization:

$H_2C_2O_4 + H_2O = H_3O^+ + HC_2O_4^-$

$1.40 - x$ x x

$6.5\cdot10^{-2} = \frac{x^2}{1.40 - x}$ $[H_2C_2O_4] = 1.40 - .27 = 1.13M$

$x = .27$

2nd ionization:

$HC_2O_4^- + H_2O = H_3O^+ + C_2O_4^{2-}$

I $.27$ $.27$ 0

C $-x$ $+x$ $+x$

E $.27 - x$ $.27 + x$ x

$6.1\cdot10^{-5} = \frac{(.27+x)(x)}{(.27-x)}$ $[HC_2O_4^-] = .27 - x$ $.27M$

$x = 6.1\cdot10^{-5}M$ $[C_2O_4^{2-}] = x = 6.1\cdot10^{-5}M$

$[H_3O^+] = .27 + x = .27M$

$pH = -\log(.27) = .569$

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1\cdot10^{-14}}{.27} = 3.7\cdot10^{-14}M$

Mar 10-8:35 AM

Calculating the pH of Basic Solutions

$pH + pOH = 14$

The key to understanding the pH of basic solutions is to recognize that, in an equilibrium sense, bases work in the same way acids do. Just as there are both strong and weak acids, there are both strong and weak bases. Strong bases completely dissociate. Using lithium hydroxide in water as an example,

$$LiOH(s) \rightarrow Li^+(aq) + OH^-(aq)$$

$.01M$ $.01$ $.01$

$\therefore pOH = -\log(.01) = 2$

$\therefore pH = 12$

Therefore, one can consider that $[OH^-] = [LiOH]_o$. Once you know $[OH^-]$, you can use K_w to calculate $[H^+]$ and pH.

Recall that all alkali hydroxides are strongly basic. Alkaline earth hydroxides are strongly basic, but somewhat less soluble than alkali hydroxides.

Weak bases react with water (we use the term "undergo hydrolysis") as described in the following reaction:

$$B(aq) + H_2O(l) = BH^+(aq) + OH^-(aq)$$

base1 acid2 acid1 base2

Mar 10-8:35 AM

Problem: Calculate the pH of a 0.350 M solution of methylamine, CH_3NH_2. The $K_b = 4.38 \times 10^{-4}$.

$$\underset{B_1}{CH_3NH_2} + \underset{A_2}{H_2O} = \underset{A_1}{CH_3NH_3^+} + \underset{B_2}{OH^-}$$

	CH_3NH_2	$CH_3NH_3^+$	OH^-
I	.350	0	0
C	$-x$	$+x$	$+x$
E	$.350-x$	x	x

$$4.38 \cdot 10^{-4} = \frac{x^2}{.350-x} \quad x = .0122\,M$$

$$\therefore [OH^-] = x = .0122\,M$$

$$pOH = -\log(.0122) = 1.91$$

$$pH = 14 - 1.91 = \underline{12.09}$$

or $$[H_3O^+] = \frac{K_w}{OH^-} = \frac{1 \cdot 10^{-14}}{.0122} = 8.20 \cdot 10^{-13}$$

$$pH = -\log(8.20 \cdot 10^{-13}) = \underline{12.09}$$

Mar 10-8:36 AM

Acid-Base Properties of Salts

Salts are ionic compounds. They dissociate in water and may exhibit acid-base behavior. The **key question** in deciding whether a salt will act as an acidic, basic, or neutral species in solution is "**What are the acid-base properties, and strengths, of each component of the salt?**"

Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$. The ions of these salts do not "react" with water; they have no acid-base properties.

Example: KCl

Ions having no acid base properties:

Li^+	Cl^-
Na^+	I^-
K^+	Br^-
Rb^+	NO_3^-

Mar 10-8:36 AM

2. Salts whose cation has neutral properties (i.e. Na^+, K^+) and whose anion is the conjugate base of a weak acid will produce a basic solution.

Example: $NaC_2H_3O_2$ $\cancel{Na}^+$ $C_2H_3O_2^-$

$$C_2H_3O_2^- + H_2O = HC_2H_3O_2 + \boxed{OH^-}$$

basic

3. Salts in which the cation is the conjugate acid of a weak base will produce an acidic solution.

Example: NH_4Cl $NH_4^+ + \cancel{Cl^-}$

$$NH_4^+ + H_2O = \underset{\text{ACID}}{\boxed{H_3O^+}} + NH_3$$

Mar 10-8:41 AM

4. For a salt where both cation and anion exhibit acid-base behavior, the overall pH is determined by comparing K_a with K_b.

NOTE: $K_w = K_a \times K_b$ (for conjugate pairs)

K_b for $NH_3 = 1.8\cdot10^{-5}$

Example: $NH_4C_2H_3O_2$ $NH_4^+ + C_2H_3O_2^-$

$NH_4^+ + H_2O = NH_3 + H_3O$ $K_a = \frac{K_w}{K_b} = \frac{1\cdot10^{-14}}{1.8\cdot10^{-5}}$

$K_a = 5.5\cdot10^{-10}$

$C_2H_3O_2^- + H_2O = HC_2H_3O_2 + OH^-$

K_a of $HC_2H_3O_2 = 1.8\cdot10^{-5}$ $K_b = \frac{K_w}{K_a} = \frac{1\cdot10^{-14}}{1.8\cdot10^{-5}}$

$K_b = 5.5\cdot10^{-10}$

since $K_a = K_b$ solution is neutral

Mar 10-8:41 AM

Problem: Using tables of constants, predict whether each of the following will create an acidic, basic, or neutral solution.

Na_3PO_4

$\cancel{Na^+} + PO_4^{3-}$

$PO_4^{3-} + H_2O = HPO_4^{2-} + OH^-$ basic

KI

$\cancel{K^+}$ $\cancel{I^-}$

$H_2O =$ pH=7 neutral

NH_4F

$K_b\ NH_3 = 1.8\cdot10^{-5}$

$K_A\ HF = 7.2\cdot10^{-4}$

$NH_4^+ + H_2O = NH_3 + H_3O^+$ $K_a = \frac{K_w}{K_b} = 5.5\cdot10^{-10}$

$F^- + H_2O = HF + OH^-$

$K_b = \frac{K_w}{K_a} = \frac{1\cdot10^{-14}}{7.2\cdot10^{-4}}$

$K_b = 1.4\cdot10^{-11}$

∴ since $K_a > K_b$

Acidic

Mar 10-8:42 AM

Problem: Calculate the pH of a 0.500 M $NaNO_2$ solution. (K_a for $HNO_2 = 4.0 \times 10^{-4}$).

$\cancel{Na^+}$ NO_2^-

base $NO_2^- + H_2O = HNO_2 + OH^-$

$$\begin{array}{lcccc} & NO_2^- & & HNO_2 & OH^- \\ I & .500 & & 0 & 0 \\ C & -x & & +x & +x \\ E & .500-x & & x & x \end{array}$$

$K_b = \frac{K_w}{K_a} = \frac{1\cdot10^{-14}}{4\cdot10^{-4}} = 2.5\cdot10^{-11}$

$2.5\cdot10^{-11} = \frac{x^2}{.500-x}$

$x = \underline{3.5}\cdot10^{-6} = [OH^-]$

$pOH = -\log(3.5\cdot10^{-6})$

$pOH = 5.\underline{46}$

$\therefore pH = 14 - 5.46 = \underline{8.54}$ ✓

Mar 10-8:42 AM

KCN

Problem: Calculate the pH of a 0.800 M ~~NH_4CN~~ solution.
The K_a for HCN = 6.2 X 10^{-10}, ~~the K_b for NH_3 = 1.8 X 10^{-5}~~.

Mar 10-8:42 AM