AP*Chemistry
The Chemistry of Acids and Bases

"ACID"--Latin word acidus, meaning sour. (lemon)
"ALKALI"--Arabic word for the ashes that come from burning certain plants; water solutions feel slippery and taste bitter. (soap)

Acids and bases are extremely important in many everyday applications: our own bloodstream, our environment, cleaning materials, and industry. (Sulfuric acid is an economic indicator!)

ACID-BASE THEORIES
❖ **ARRHENIUS DEFINITION**
   ▪ **acid--**donates a hydrogen ion (H^+) in water
   ▪ **base**--donates a hydroxide ion in water (OH^-)
This theory was limited to substances with those "parts"; ammonia is a MAJOR exception!

❖ **BRONSTED-LOWRY DEFINITION**
   ▪ **acid--**donates a proton in water
   ▪ **base--**accepts a proton in water
This theory is better; it explains ammonia as a base! This is the main theory that we will use for our acid/base discussion.
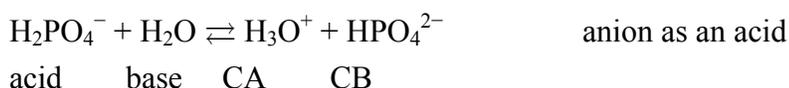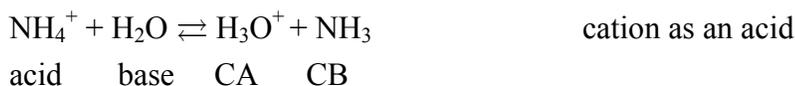
❖ **LEWIS DEFINITION**
   ▪ **acid--**accepts an electron pair
   ▪ **base**--donates an electron pair
This theory explains **all** traditional acids and bases plus a host of coordination compounds and is used widely in organic chemistry. Uses coordinate covalent bonds.
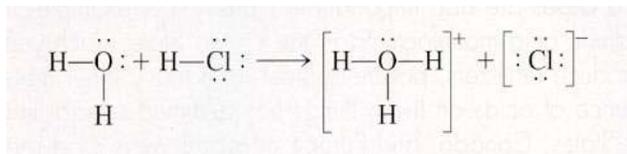
THE BRONSTED-LOWRY CONCEPT OF ACIDS AND BASES
Using this theory, you should be able to write weak acid/base dissociation equations and identify acid, base, conjugate acid and conjugate base.
   ▪ **conjugate acid-base pair**--A pair of compounds that differ by the presence of one H^+ unit. This idea is critical when it comes to understanding buffer systems. Pay close attention now and it will pay off later!

$HNO_3 + H_2 \rightarrow H_3O^+ + NO_3^-$ neutral compound as an acid
acid   base   CA   CB

$NH_4^+ + H_2O \rightleftarrows H_3O^+ + NH_3$ cation as an acid
acid   base   CA   CB

$H_2PO_4^- + H_2O \rightleftarrows H_3O^+ + HPO_4^{2-}$ anion as an acid
acid   base   CA   CB

In each of the acid examples---notice the formation of H_3O^+ -- this species is named the **hydronium ion**. It lets you know that the solution is **acidic**!

      (*hydronium*, H_3O^+--H^+ riding piggy-back on a water molecule; water is polar and the
      + charge of the "naked" proton is greatly attracted to Mickey's chin!)

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ neutral compound
base   acid   CA   CB

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ anion
base   acid   CA   CB

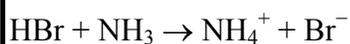$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ anion
base   acid   CA   CB

Notice the formation of OH^- in each of the alkaline examples. This species is named the **hydroxide ion**. It lets you know that the resulting solution is **basic**!

You try!!

Exercise 1
a) In the following reaction, identify the acid on the left and its CB on the right. Similarly identify the base on the left and its CA on the right.

$HBr + NH_3 \rightarrow NH_4^+ + Br^-$

b) What is the conjugate base of H_2S?

c) What is the conjugate acid of NO_3^-?
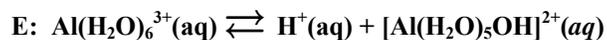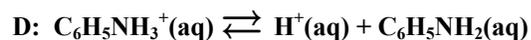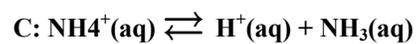

❖ **ACIDS DONATE ONLY ONE PROTON AT A TIME!!!**

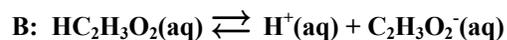   ➢ **monoprotic**--acids donating one H^+ (ex. $HC_2H_3O_2$)
    ➢ **diprotic**--acids donating two H^+'s (ex. $H_2C_2O_4$)
    ➢ **polyprotic**--acids donating many H^+'s (ex. H_3PO_4)

    ➢ **polyprotic bases**--accept more than one H^+; anions with −2 and −3 charges (ex. PO_4^{3-} ; HPO_4^{2-})

➤ **Amphiprotic or amphoteric** --molecules or ions that can behave as EITHER acids or bases; water, anions of weak acids (look at the examples above—sometimes water was an acid, sometimes it acted as a base)

Exercise 2   Acid Dissociation (Ionization) Reactions

Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids.

a. Hydrochloric acid (HCl)

b. Acetic acid ($HC_2H_3O_2$)

c. The ammonium ion (NH_4^+)

d. The anilinium ion ($C_6H_5NH_3^+$)

e. The hydrated aluminum(III) ion $[Al(H_2O)_6]^{3+}$

A: $HCl(aq) \rightleftarrows H^+(aq) + Cl^-(aq)$

B: $HC_2H_3O_2(aq) \rightleftarrows H^+(aq) + C_2H_3O_2^-(aq)$

C: $NH4^+(aq) \rightleftarrows H^+(aq) + NH_3(aq)$

D: $C_6H_5NH_3^+(aq) \rightleftarrows H^+(aq) + C_6H_5NH_2(aq)$

E: $Al(H_2O)_6^{3+}(aq) \rightleftarrows H^+(aq) + [Al(H_2O)_5OH]^{2+}(aq)$
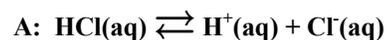
RELATIVE STRENGTHS OF ACIDS AND BASES

Strength is determined by the position of the "dissociation" equilibrium.

> **Strong** acids/strong bases
> 1. dissociates completely in water
> 2. have very large dissociation or K values

Before dissociation
After dissociation, at equilibrium

HA → H⁺ A⁻

Strong ← → Weak

(a)

HA → HA

> **Weak** acids/weak bases
> 1. dissociate only to a slight extent in water
> 2. dissociation constant is very small

H⁺ A⁻

Do Not confuse concentration with strength!

(b)
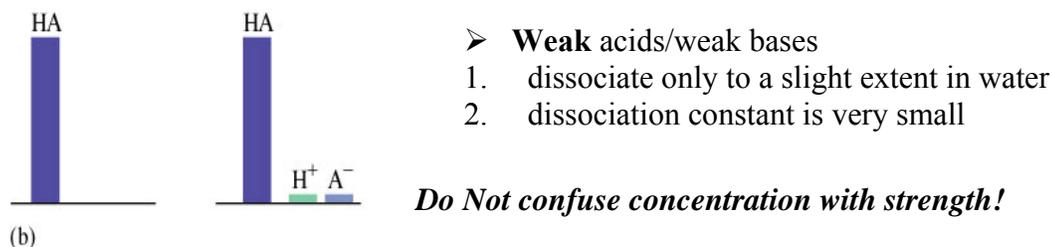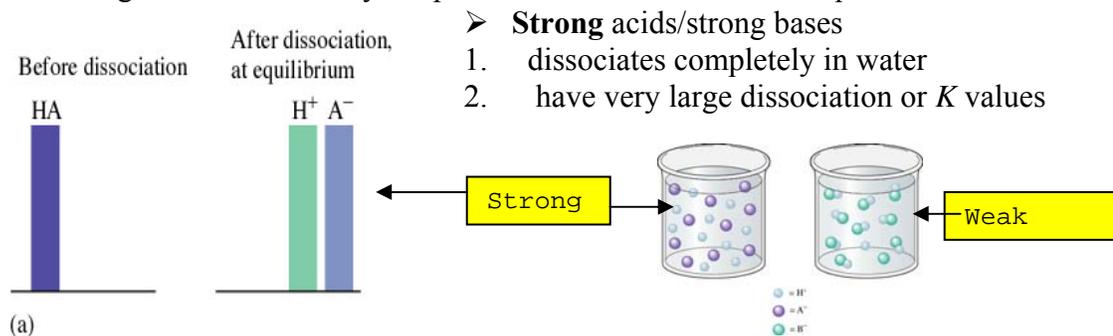
❖ **STRONG ACIDS: Memorize these SIX**
   > Hydrohalic acids: HCl, HBr, HI—note HF is missing!
   > Nitric: HNO_3
   > Sulfuric: H_2SO_4
   > Perchloric: $HClO_4$

Table 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Hydrochloric Acid

The label on a bottle of concentrated hydrochloric acid.
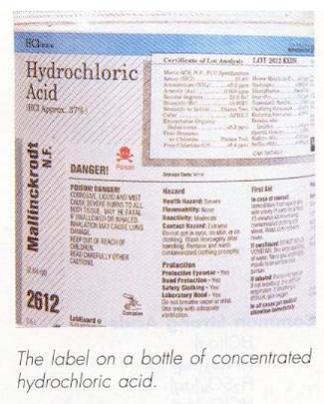
The **more oxygen** present in the polyatomic ion of an oxyacid, the **stronger** its acid **WITHIN** that group. That's a trend, but not an explanation. So, why? First, notice that the H of the acid is bound to an oxygen and NOT any other nonmetal present. Oxygen is very electronegative and attracts the electrons of the O−H bonds toward itself. If you add more oxygens, then this effect is magnified and there is increasing electron density in the region of the molecule that is opposite the H. The added electron density weakens the bond, thus less energy is required to break the bond and the acid dissociates more readily which we describe as "strong".
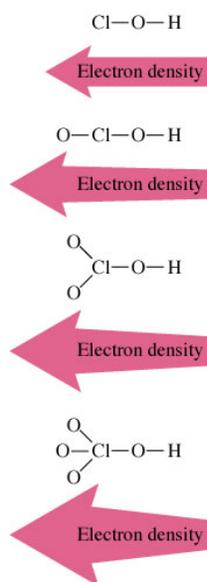

Table 14.8 Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$	H—O—Cl, with O above and two O's	Large ($\sim 10^7$)
$HClO_3$	H—O—Cl, with O above and O below	~1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
$HClO$	H—O—Cl	3.5×10^{-8}
H_2SO_4	H—O—S—O with O—H and O	Large
H_2SO_3	H—O—S with O—H and O	1.5×10^{-2}
HNO_3	H—O—N with O above and O below	Large
HNO_2	H—O—N—O	4.0×10^{-4}

❖ **STRONG BASES**
  ➢ Hydroxides OR oxides of IA and IIA metals (except Mg and Be)
      o Solubility plays a role (those that are very soluble are strong!)

❖ **THE STRONGER THE ACID THE WEAKER ITS CB,** *the converse is also true.*
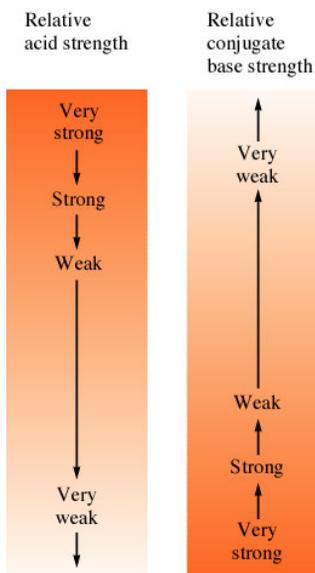

Table 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

❖ WEAK ACIDS AND BASES:

➢ *The vast majority of acid/bases are weak.* Remember, this means they do not ionize much.

That means a equilibrium is established and it lies far to the left (reactant favored).
The equilibrium expression for acids is known as the K_a **(the acid dissociation constant)**. It is set up the same way as any other equilibrium expression. Many common weak acids are oxyacids, like phosphoric acid and nitrous acid. Other common weak acids are organic acids— those that contain a carboxyl group, the COOH group, like acetic acid and benzoic acid.
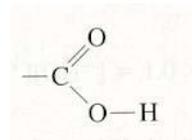
For weak acid reactions: $\quad HA + H_2O \rightleftharpoons H_3O^+ + A^-$
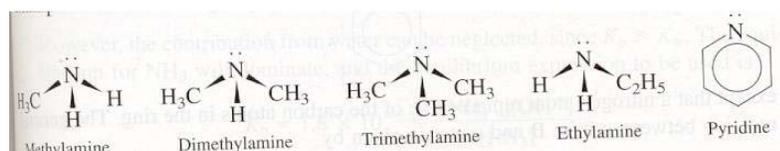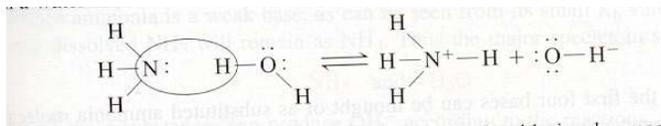
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad << 1$$

Table 14.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

*The units of K_a are customarily omitted.

Increasing acid strength ↑

➢ Write the K_a expression for acetic acid. (Note: Water is a pure liquid and is thus, left out of the equilibrium expression.)

➢ Weak bases (bases without OH^-) react with water to produce a hydroxide ion. Common examples of weak bases are ammonia (NH_3), methylamine (CH_3NH_2), and ethylamine ($C_2H_5NH_2$). The lone pair on N forms a bond with a H^+. Most weak bases involve N.

Methylamine   Dimethylamine   Trimethylamine   Ethylamine   Pyridine

The equilibrium expression for **bases** is known as the K_b.

for weak base reactions: $B + H_2O \rightleftharpoons HB^+ + OH^-$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \quad << 1$$

Table 14.3 Values of K_b for Some Common Weak Bases

| Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

♦ Write the K_b expression for ammonia.

♦ Notice that K_a and K_b expressions look very similar. The difference is that a base produces the hydroxide ion in solution, while the acid produces the hydronium ion in solution.
♦ Another note on this point: H^+ and H_3O^+ are both equivalent terms here. Often water is left completely out of the equation since it does not appear in the equilibrium. This has become an accepted practice. (* However, water is very important in causing the acid to dissociate.)

Exercise 3   **Relative Base Strength**

Using table 14.2, arrange the following species according to their strength as bases:

H_2O, F^-, Cl^-, NO_2^-, and CN^-.

$Cl^- < H_2O < F^- < NO_2^- < CN^-$
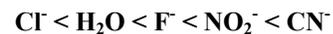
WATER, THE HYDRONIUM ION, AUTO-IONIZATION, AND THE pH SCALE

➢ Fredrich Kohlrausch, around 1900, found that no matter how pure water is, it still conducts a minute amount of electric current. This proves that water self-ionizes.

- Since the water molecule is amphoteric, it may dissociate with itself to a slight extent.
- *Only about 2 in a billion water molecules are ionized at any instant!*

$$H_2O(l) \quad + \qquad H_2O(l) \qquad \rightleftharpoons \qquad H_3O^+(aq) \quad + \quad OH^-(aq)$$
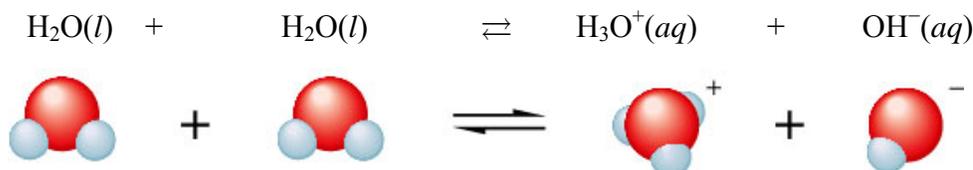
- The equilibrium expression used here is referred to as the **autoionization constant for water, K_w**
- In pure water or dilute aqueous solutions, the concentration of water can be considered to be a constant (55.6 M), so we include that with the equilibrium constant and write the expression as:

$$K_w = [H_3O^+][OH^-] = 1.008 \times 10^{-14} \text{ @ } 25°C = K_a \times K_b$$

- ♦ Knowing this value allows us to calculate the OH^- and H^+ concentration for various situations.
- ♦ $[OH^-] = [H^+]$ solution is neutral (in pure water, each of these is 1.0×10^{-7})
- ♦ $[OH^-] > [H^+]$ solution is basic
- ♦ $[OH^-] < [H^+]$ solution is acidic

Exercise 5   **Autoionization of Water**

At 60°C, the value of K_w is 1×10^{-13}.

a. Using Le Chatelier's principle, predict whether the reaction below is exothermic or endothermic.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 60°C.

<div align="right">

**A: endothermic**

B: $[H^+] = [OH^-] = 3 \times 10^{-7} M$

</div>

The pH Scale

❖ Used to designate the $[H^+]$ in most aqueous solutions where $[H^+]$ is small.

$$pH = -\log [H^+]$$
$$pOH = -\log [OH^-]$$
$$pH + pOH = 14$$

If pH is between zero and 6.999, the solution is acidic, if pH is 7.000, the solution is neutral and if the pH is above 7.000, the solution is basic.

❖ Reporting the correct number of sig. figs on a pH is problematic since it is a logarithmic scale. The rule is to report as many decimal places on a pH as there are in the least accurate measurement you are given.

❖ Example: The problem states a 1.15 M solution blah, blah, blah. That is your cue to report a pH with 3 decimal places. If the problem had stated a 1.2 M solution blah, blah, blah, then you would report your calculated pH to 2 decimal places. How did this ever get started? If you care…read the next bullet…otherwise go directly to Exercise 6!

❖ In the old days, before calculators (Can you imagine?), students used log tables to work problems involving logarithms. If the logarithm was 7.45, then the "7" was the characteristic and the ".45" part was the mantissa. In fact, it is the mantissa that communicates the accuracy of the measurement. The characteristic is simply a place holder.
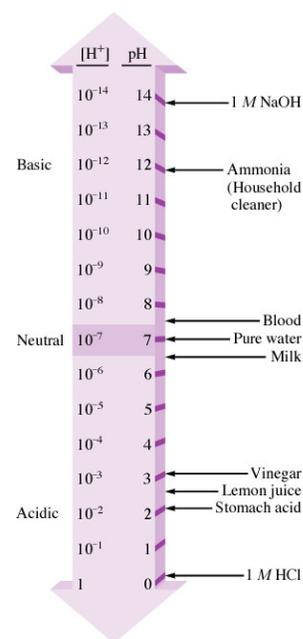
Exercise 6   **Calculating [H+] and [OH⁻]**

Calculate either the $[H^+]$ or $[OH^-]$ from the information given for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

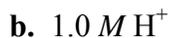**a.** $1.0 \times 10^{-5}\, M\ OH^-$

b. $1.0 \times 10^{-7}\, M\ OH^-$

c. $10.0\, M\ H^+$

A: $[H^+] = 1.0 \times 10^{-9}\, M$, **basic**
B: $[H^+] = 1.0 \times 10^{-7}\, M$, **neutral**
C: $[OH^-] = 1.0 \times 10^{-15}\, M$, **acidic**

Exercise 7   **Calculating pH and pOH**

Calculate pH and pOH for each of the following solutions at 25°C.

a. $1.0 \times 10^{-3} \, M \, OH^-$

b. $1.0 \, M \, H^+$

A: pH = 11.00
pOH = 3.00
B: pH = 0.00
pOH = 14.00

Exercise 8   **Calculating pH**

The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample.

pOH = 6.59
$[H^+] = 3.9 \times 10^{-8} \, M$
$[OH^-] = 2.6 \times 10^{-7} \, M$

Exercise 9   **pH of Strong Acids**

a. Calculate the pH of $0.10 \, M \, HNO_3$.

b. Calculate the pH of $1.0 \times 10^{-10} \, M \, HCl$.

A: pH = 1.00
B: pH = 10.00

Exercise 10 **The pH of Strong Bases**

Calculate the pH of a 5.0×10^{-2} M NaOH solution.

pH = 12.70

❖ **Calculating pH of Weak Acid Solutions**
Calculating pH of weak acids involves setting up an equilibrium. Always start by writing the balanced equation, setting up the acid equilibrium expression (K_a), defining initial concentrations, changes, and final concentrations in terms of x, substituting values and variables into the K_a expression and solving for x. Use the **RICE TABLE** method you learned in general equilibrium!

Example
Calculate the pH of a 1.00×10^{-4} M solution of acetic acid. The K_a of acetic acid is 1.8×10^{-5}.

	Reaction	$HC_2H_3O_2$	$\rightleftarrows$	H^+	+	$C_2H_3O_2^-$
Initial		1.00×10^{-4}		0		0
Change		$-x$		$+x$		$+x$
Equilibrium		$(1.00 \times 10^{-4}) - x$		x		x

$$K_a = \frac{\left[H^+\right]\left[C_2H_3O_2^-\right]}{HC_2H_3O_2} = 1.8 \times 10^{-5} = \frac{x^2}{1 \times 10^{-4} - x}$$

See that $-x$ term in the denominator? That is your invitation to cross multiply and distribute the K_a value across the term so that you get $x^2 = 1.8 \times 10^{-9} - 1.8 \times 10^{-5}x$; collect like terms and use either the solver on your graphing calculator or a quadratic formula solving program you've loaded on your calculator (all of this to avoid arithmetic mistakes!) to solve for x. You should determine that $x = [H^+] = 3.44 \times 10^{-4}$ and that the pH $= -\log (3.44 \times 10^{-4}) = 3.46$ (2 SF).

Often, the $-x$ term in a K_a expression can be neglected. That simplifies the math tremendously since you are now spared the tedium of having to use the quadratic formula.

How do you know when to neglect x? Easy. Look at the original concentration and compare it to 100 K_a (or 100 K_b). IF the initial concentration is large by comparison, you can neglect subtracting the x term. We could not neglect x in the example we just worked since 100 K_a for acetic acid would equal 1.8×10^{-3} or 0.0018 which is too close to our initial acid concentration of 0.0001.

Need proof?

Suppose our initial concentration had been 0.10 M for the acetic acid in the example problem we just worked. For acetic acid, $100K_a = 1.8 \times 10^{-3}$ or 0.0018. That's essentially subtracting zero from 0.10 M. Aside from that if you did subtract it, you'd still follow the "least decimal place" subtraction sig. fig. rule and report 0.10 M as your answer to the subtraction.

OK, I'll humor you and apply the quadratic formula to the example we just worked changing the initial concentration to 0.10 M. First I'll do the quadratic formula and then I'll work it by "*neglecting x*".

Example
Calculate the pH of a 10.10 M solution of acetic acid. The K_a of acetic acid is 1.8×10^{-5}.

Reaction	$HC_2H_3O_2$	$\rightleftarrows$	H^+	+	$C_2H_3O_2^-$
Initial	0.10		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.10 - x$		x		x

$$K_a = \frac{\left[H^+\right]\left[C_2H_3O_2^-\right]}{HC_2H_3O_2} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

By cross multiplying and NOT neglecting x, you get $x^2 = 1.8 \times 10^{-6} - 1.8 \times 10^{-5}x$; collect like terms and use either the solver on your graphing calculator or a quadratic formula solving program you've loaded on your calculator (all of this to avoid arithmetic mistakes!) to solve for x. You should determine that $x = \left[H^+\right] = 0.0013327$ (way too many sig. figs, I know!)

and that the pH $= -\log(0.0013327) = 2.88$ (2 SF)

Had we "*neglected x*", the math simplifies to
$$K_a = \frac{\left[H^+\right]\left[C_2H_3O_2^-\right]}{HC_2H_3O_2} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - \cancel{x}} \quad \text{and} \quad x^2 = 1.8 \times 10^{-6}$$

So, take the square root of each side to get
$$\sqrt{x^2} = \sqrt{1.8 \times 10^{-6}}$$
$$x = 0.00134 = \left[H^+\right]$$

pH $= -\log(.001341) = 2.87$ (2 SF) which is mighty, mighty close, so it is a really good approximation.

So, what's the good news? The AP exam does not have equilibrium problems that require the quadratic formula. Feel better? No promises about your homework, though! ☺

- List the major species in the solution.
- Choose the species that can produce H^+, and write balanced equations for the reactions producing H^+.
- Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+.
- Write the equilibrium expression for the dominant equilibrium.
- List the initial concentrations of the species participating in the dominant equilibrium.
- Define the change needed to achieve equilibrium; that is, define x.
- Write the equilibrium concentrations in terms of x.
- Substitute the equilibrium concentrations into the equilibrium expression.
- Solve for x the "easy" way; that is, by assuming that $[HA]_0 - x \approx [HA]_0$.
- Use the 5% rule to verify whether the approximation is valid.
- Calculate $[H^+]$ and pH.

Exercise 11   **The pH of Weak Acids**

The hypochlorite ion (OCl^-) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than Cl^-, for example) and forms the weakly acidic hypochlorous acid ($HOCl$, $K_a = 3.5 \times 10^{-8}$). Calculate the pH of a 0.100 M aqueous solution of hypochlorous acid.

pH = 4.23

❖ **Determination of the pH of a Mixture of Weak Acids**

➤ Only the acid with the largest K_a value will contribute an appreciable $[H^+]$. Determine the pH based on this acid and ignore any others.

Exercise 12   **The pH of Weak Acid Mixtures**

Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO$_2$ ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN$^-$) in this solution at equilibrium.

pH = 1.35
$[CN^-] = 1.4 \times 10^{-8}\ M$

Exercise 13   **Calculating Percent Dissociation**

Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solutions.

a. 1.00 M HC$_2$H$_3$O$_2$

b. 0.100 M HC$_2$H$_3$O$_2$

A: = 0.42 %
B: = 1.3 %

Exercise 14 **Calculating K_a from Percent Dissociation**

Lactic acid ($HC_3H_5O_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 *M* aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

$K_a = 1.4 \times 10^{-4}$

❖ Determination of the pH of a **weak base** is very similar to the determination of the pH of a weak acid. Follow the same steps. Remember, however, that x is the $[OH^-]$ and taking the negative log of x will give you the **pOH** and not the pH!

Exercise 15 **The pH of Weak Bases I**

Calculate the pH for a 15.0 *M* solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

pH = 12.20

Exercise 16 **The pH of Weak Bases II**
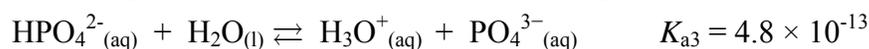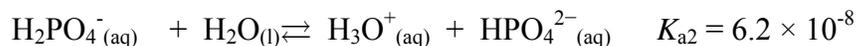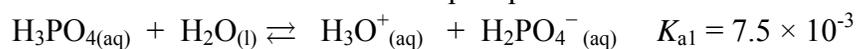
Calculate the pH of a 1.0 M solution of methylamine ($K_b = 4.38 \times 10^{-4}$).

<div align="right">**pH = 12.32**</div>

❖ **Calculating pH of polyprotic acids**

➢ Acids with more than one ionizable hydrogen will ionize in steps. Each dissociation has its own K_a value.

➢ The **first** dissociation will be the **greatest** and subsequent dissociations will have much smaller equilibrium constants. As each H^+ is removed, the remaining acid gets weaker and therefore has a smaller K_a. As the negative charge on the acid increases it becomes more difficult to remove the positively charged proton.

  ▪ Example: Consider the dissociation of phosphoric acid.

$$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-_{(aq)} \qquad K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}_{(aq)} \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}_{(aq)} \qquad K_{a3} = 4.8 \times 10^{-13}$$

➢ Looking at the K_a values, it is obvious that only the first dissociation will be important in determining the pH of the solution.

Table 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

> Except for H_2SO_4, polyprotic acids have K_{a2} and K_{a3} values so much weaker than their K_{a1} value that the 2nd and 3rd (if applicable) dissociation can be ignored. The $[H^+]$ obtained from this 2nd and 3rd dissociation is negligible compared to the $[H^+]$ from the 1st dissociation. Because H_2SO_4 is a strong acid in its first dissociation and a weak acid in its second, we need to consider both if the concentration is more dilute than 1.0 M. The quadratic equation is needed to work this type of problem.

Exercise 17   **The pH of a Polyprotic Acid**

Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

<div align="right">

pH = 0.72
$[H_3PO_4]$ = 4.8 M
$[H_2PO_4^-]$ = 0.19 M
$[HPO_4^{2-}]$ = 6.2 × 10^{-8} M
$[PO_4^{3-}]$ = 1.6 × 10^{-19} M

</div>

Exercise 18   **The pH of a Sulfuric Acid**

Calculate the pH of a 1.0 M H_2SO_4 solution.

<div align="right">

pH = 0.00

</div>

<div style="border: 1px solid black;">

**Exercise 19**   **The pH of a Sulfuric Acid**

Calculate the pH of a 1.0×10^{-2} M H_2SO_4 solution.

pH = 1.84

</div>

❖ ACID-BASE PROPERTIES OF SALTS: HYDROLYSIS (Splitting of water)

Salts are produced when an acid and base react. Salts are **not** always neutral. Some hydrolyze with water to produce aqueous solutions with pHs other than 7.00.

> **Neutral Salts**--Salts that are formed from the cation of a strong base reacting with the anion of a strong acid are neutral. Beware of solubility issues! One salt such is $NaNO_3$. Think about which acid reacted with which base to form the salt…if both the acid and base are strong, then the salt is neutral.

> **Basic Salts**--Salts that are formed from the cation of a strong base reacting with the anion of a weak acid are basic. Again, beware of solubility issues! The anion hydrolyzes the water molecule to produce hydroxide ions and thus a basic solution. $K_2C_2H_3O_2$ should be basic since $C_2H_3O_2^-$ is the CB of the weak acid $HC_2H_3O_2$, while K^+ does not hydrolyze appreciably.

$$C_2H_3O_2^- + H_2O \rightleftharpoons OH^- + HC_2H_3O_2$$
$$\text{strong base} \quad \text{weak acid}$$
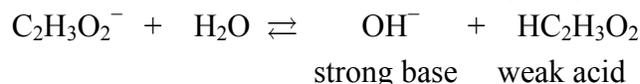
> **Acid Salts**-   Salts that are formed from the cation of a weak base reacting with the anion of a strong acid are acidic. The cation hydrolyzes the water molecule to produce hydronium ions and thus an acidic solution. NH_4Cl should be weakly acidic, since NH_4^+ hydrolyzes to give an acidic solution, while Cl^- does not hydrolyze.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$
$$\text{strong acid} \quad \text{weak base}$$
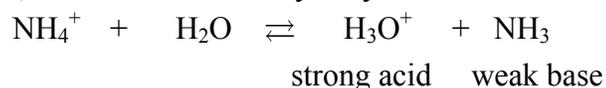
- If both the cation and the anion contribute to the pH situation, compare K_a to K_b.
- If K_b is larger, basic! The converse is also true.

Table 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Here's how to think this through:

1. Look at the salt and ask yourself which acid and which base reacted to form it?

2. Ask yourself "strong or weak?" for each.

3. Embrace the fact that "strong wins" and predict whether the salt is acidic or basic based on that victory.

   a. If you predict basic, write $\rightleftharpoons OH^-$

   b. If you predict acidic, write $\rightleftharpoons H^+$

4. Relish in the fact that "strong is a spectator". Which means the remaining ion of the salt is the reactant along with water.

5. Write water as HOH to make it easier to see how the hydroxide or hydrogen ion was formed.

Example:
Question: What is the qualitative pH of $Fe(NO_3)_3$?

1. Which acid reacted? Nitric
2. Strong or weak? Strong
3. Which base reacted? Iron(III) hydroxide
4. Strong or weak? Weak

Strong wins! $\therefore$ acidic so we write:

$$+ HOH \rightleftharpoons H^+ \quad \text{to get started}$$

Strong is also a spectator so, cross out the spectator and the remaining ion is the other reactant; Fe(~~NO₃~~)₃

Complete hydrolysis reaction: $Fe^{3+} + 3\ HOH \rightleftharpoons 3\ H^+ + Fe(OH)_3$
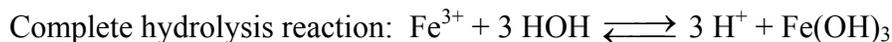
Exercise 20   **The Acid-Base Properties of Salts**

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. Prove with appropriate equations.

a. $NaC_2H_3O_2$

b. NH_4NO_3

c. $Al_2(SO_4)_3$
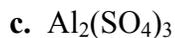
Exercise 21   **Salts as Weak Bases**

Calculate the pH of a 0.30 M NaF solution. The K_a value for HF is 7.2×10^{-4}.

pH = 8.31

Exercise 22   **Salts as Weak Acids I**

Calculate the pH of a 0.10 M NH$_4$Cl solution. The K_b value for NH$_3$ is 1.8×10^{-5}.

pH = 5.13

Exercise 23   **Salts as Weak Acids II**

Calculate the pH of a 0.010 M AlCl$_3$ solution. The K_a value for Al(H$_2$O)$_6^{3+}$ is 1.4×10^{-5}.
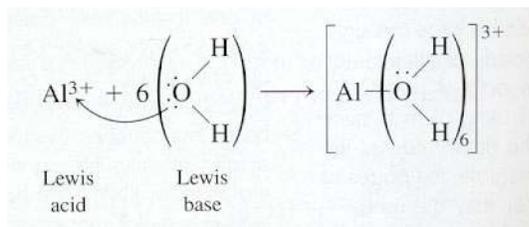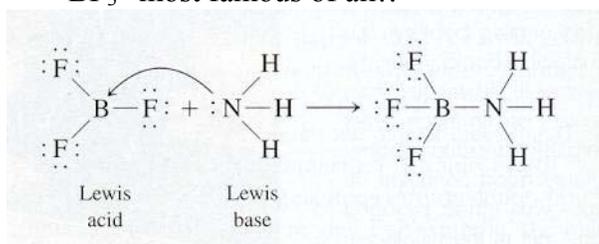
pH = 3.43

❖ THE LEWIS CONCEPT OF ACIDS AND BASES

➢ **acid**--can accept a pair of electrons to form a coordinate covalent bond
➢ **base**--can donate a pair of electrons to form a coordinate covalent bond

Yes, this is the dot guy and the structures guy--he was extremely busy making your life difficult!
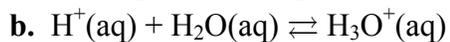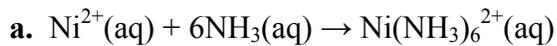
BF_3--most famous of all!!

Exercise 24
Tell whether each of the following is a Lewis acid or base: Draw structures as proof.
a) PH_3
b) BCl_3
c) H_2S
d) SF_4

Exercise 25   **Lewis Acids and Basis**

For each reaction, identify the Lewis acid and base.

a. $Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq)$
b. $H^+(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq)$

A: **Lewis acid = nickel(II) ion**
Lewis base = ammonia
B: **Lewis acid = proton**
Lewis base = water molecule

Solving Acid–Base Problems

STEP 1
List the major species in solution.

STEP 2
Look for reactions that can be assumed to go to completion, for example, a strong acid dissociating or H^+ reacting with OH^-.

STEP 3
For a reaction that can be assumed to go to completion:
a. Determine the concentration of the products.
b. Write down the major species in solution after the reaction.

STEP 4
Look at each major component of the solution and decide if it is an acid or a base.

STEP 5
Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.
a. Write the equation for the reaction and the equilibrium expression.
b. Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, etc.).
c. Define x.
d. Compute the equilibrium concentrations in terms of x.
e. Substitute the concentrations into the equilibrium expression, and solve for x.
f. Check the validity of the approximation.
g. Calculate the pH and other concentrations as required.

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid–base problems systematically, the more complex cases will be much easier to manage.