



# 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

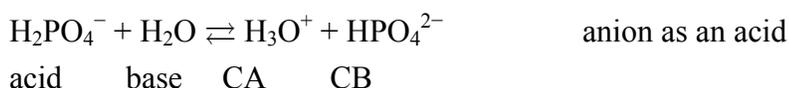
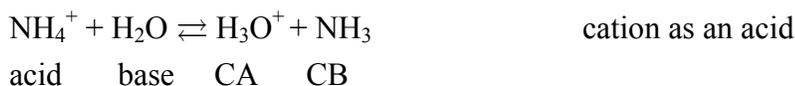
- **acid**--accepts an electron pair
- **base**--donates an electron pair

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

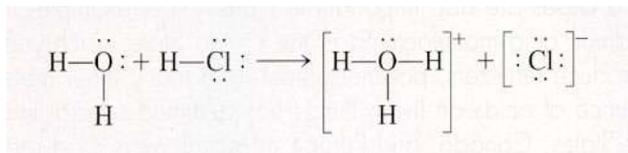
Using this theory, you should be able to write weak acid/base dissociation equations and identify acid, base, conjugate acid and conjugate base.

- **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!



In each of the acid examples---notice the formation of  $\text{H}_3\text{O}^+$  -- this species is named the **hydronium ion**. It lets you know that the solution is **acidic!**

(*hydronium*,  $\text{H}_3\text{O}^+$ -- $\text{H}^+$  riding piggy-back on a water molecule; water is polar and the + charge of the “naked” proton is greatly attracted to Mickey's chin!)

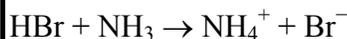


Notice the formation of  $\text{OH}^-$  in each of the alkaline examples. This species is named the **hydroxide ion**. It lets you know that the resulting solution is **basic!**

**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.



b) What is the conjugate base of  $\text{H}_2\text{S}$ ?

c) What is the conjugate acid of  $\text{NO}_3^-$ ?

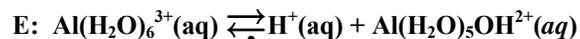
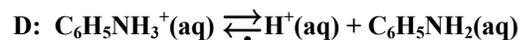
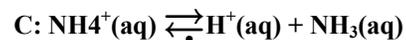
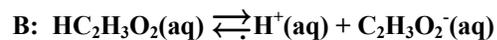
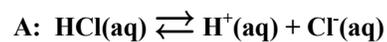
### ❖ ACIDS DONATE ONLY ONE PROTON AT A TIME!!!

- **monoprotic**--acids donating one  $\text{H}^+$  (ex.  $\text{HC}_2\text{H}_3\text{O}_2$ )
- **diprotic**--acids donating two  $\text{H}^+$ 's (ex.  $\text{H}_2\text{C}_2\text{O}_4$ )
- **polyprotic**--acids donating many  $\text{H}^+$ 's (ex.  $\text{H}_3\text{PO}_4$ )
- **polyprotic bases**--accept more than one  $\text{H}^+$ ; anions with  $-2$  and  $-3$  charges (ex.  $\text{PO}_4^{3-}$ ;  $\text{HPO}_4^{2-}$ )
- **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.

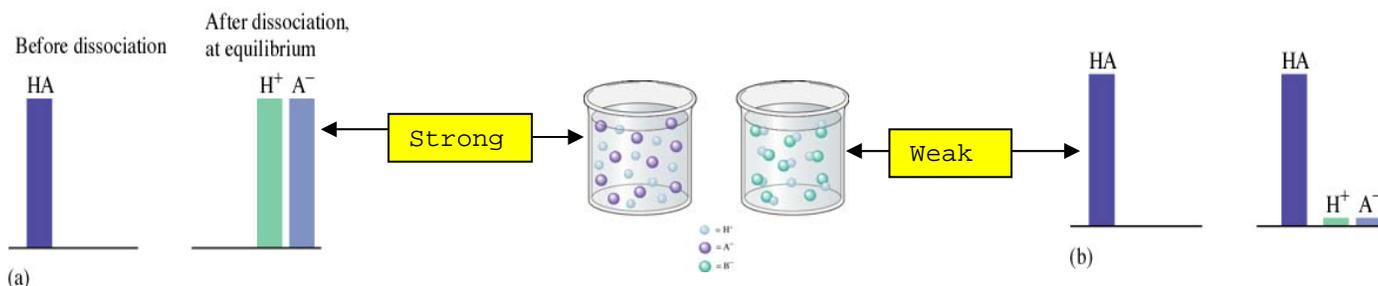
- Hydrochloric acid (HCl)
- Acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)
- The ammonium ion (NH<sub>4</sub><sup>+</sup>)
- The anilinium ion (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>)
- The hydrated aluminum(III) ion [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>



## 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



- **Weak acids/weak bases**
  1. dissociate only to a slight extent in water
  2. have very small dissociation or  $K$  values

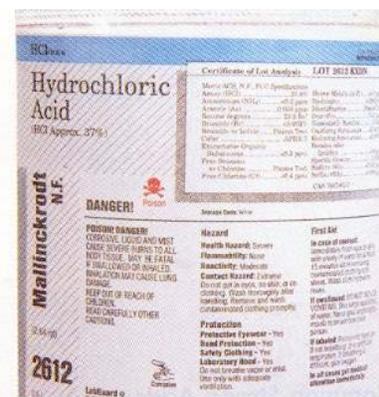
**Do Not confuse concentration with strength!**

### ❖ STRONG ACIDS: Memorize these SIX

- Hydrohalic acids: HCl, HBr, HI—note HF is missing!
- Nitric:  $\text{HNO}_3$
- Sulfuric:  $\text{H}_2\text{SO}_4$
- Perchloric:  $\text{HClO}_4$

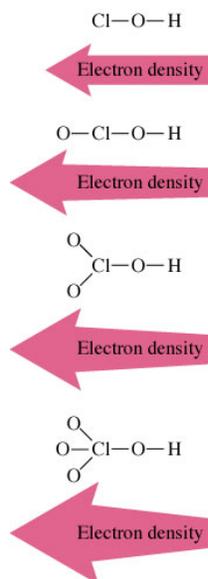
**Table 14.7** Bond Strengths and Acid Strengths for Hydrogen Halides

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



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 to the central atom, 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 polarizes the bond, thus weakens the bond, thus less energy is required to break the bond and the acid dissociates more readily which we describe as “strong”.

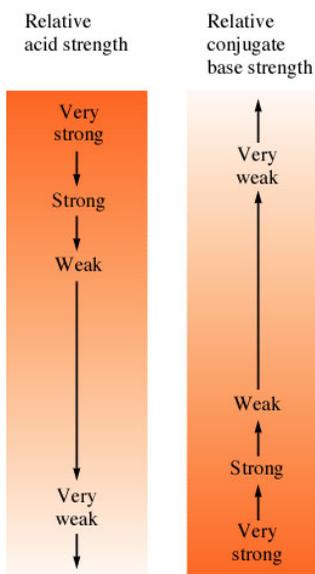


Oxyacid	Structure	$K_a$ Value
$\text{HClO}_4$		Large ( $\sim 10^7$ )
$\text{HClO}_3$		$\sim 1$
$\text{HClO}_2$		$1.2 \times 10^{-2}$
$\text{HClO}$		$3.5 \times 10^{-8}$
$\text{H}_2\text{SO}_4$		Large
$\text{H}_2\text{SO}_3$		$1.5 \times 10^{-2}$
$\text{HNO}_3$		Large
$\text{HNO}_2$		$4.0 \times 10^{-4}$

### ❖ STRONG BASES

- Hydroxides OR oxides of IA and IIA metals (except Mg and Be)
  - Solubility plays a role (those that are very soluble are strong!)

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



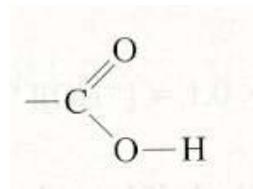
Property	Strong Acid	Weak Acid
$K_a$ value	$K_a$ is large	$K_a$ is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of $\text{H}^+$ compared with original concentration of HA	$[\text{H}^+] \approx [\text{HA}]_0$	$[\text{H}^+] \ll [\text{HA}]_0$
Strength of conjugate base compared with that of water	$\text{A}^-$ much weaker base than $\text{H}_2\text{O}$	$\text{A}^-$ much stronger base than $\text{H}_2\text{O}$

## ❖ WEAK ACIDS AND BASES:

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

That means an 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:  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \ll 1$$

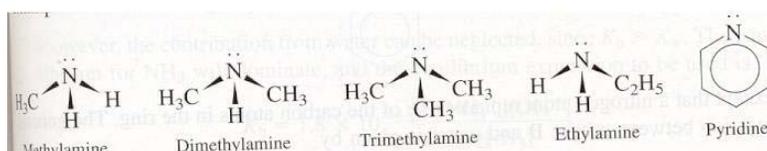
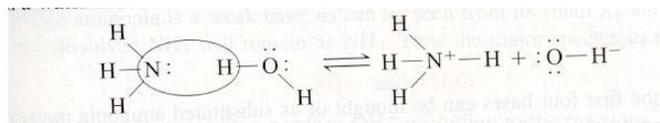
**Table 14.2** Values of  $K_a$  for Some Common Monoprotic Acids

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

\*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.



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



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

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

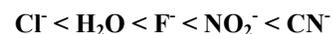
- ◆ Write the  $K_b$  expression for ammonia.
- ◆ Notice that  $K_a$  and  $K_b$  expressions look very similar. The difference is that a base produces the hydroxide ion in solution, while the acid produces the hydronium ion in solution.
- ◆ Another note on this point:  $H^+$  and  $H_3O^+$  are both 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

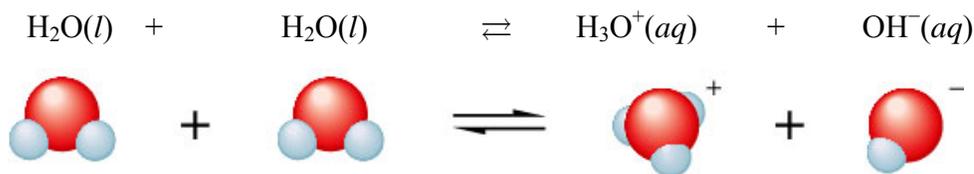
Using table 14.2, arrange the following species according to their strength as bases:

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



## 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!*



- 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:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.008 \times 10^{-14} @ 25^\circ\text{C} = K_a \times K_b$$

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

### Exercise 5

### Autoionization of Water

At  $60^\circ\text{C}$ , the value of  $K_w$  is  $1 \times 10^{-13}$ .

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



- b. Calculate  $[\text{H}^+]$  and  $[\text{OH}^-]$  in a neutral solution at  $60^\circ\text{C}$ .

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

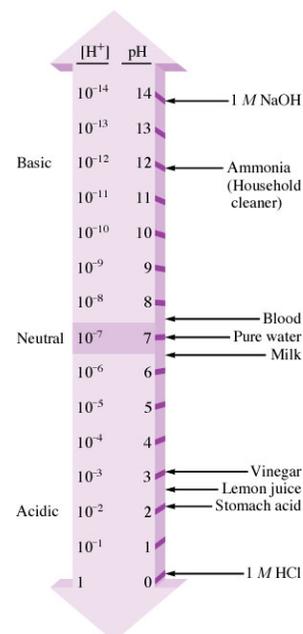
## The pH Scale

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

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ \text{pOH} &= -\log [OH^-] \\ \text{pH} + \text{pOH} &= 14 \end{aligned}$$

If pH is between zero and 6.999, the solution is acidic, if pH is 7.00, the solution is neutral and if the pH is above 7.00, 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...or the explanation in the appendix of your text...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 determined to be 7.45, then the “7” is the *characteristic* and the “.45” part is the *mantissa*. In fact, it is the *mantissa* that communicates the accuracy of the measurement of a logarithm. The characteristic is simply a place holder.



### Exercise 6 Calculating $[H^+]$ and $[OH^-]$

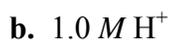
Calculate either the  $[H^+]$  or  $[OH^-]$  from the information given for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

- $1.0 \times 10^{-5} M OH^-$
- $1.0 \times 10^{-7} M OH^-$
- $10.0 M H^+$

**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: 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**

**$[H^+] = 3.9 \times 10^{-8}$**

**$[OH^-] = 2.6 \times 10^{-7} M$**

**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 = 7.00**

**Exercise 10****The pH of Strong Bases**

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

pH = 12.70

❖ **Calculating pH of Weak Acid Solutions**

Calculating pH of weak acids involves setting up an equilibrium RICE table. 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  $x$ .

**Example**

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

Reaction	$\text{HC}_2\text{H}_3\text{O}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	$1.00 \times 10^{-4}$		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$(1.00 \times 10^{-4}) - x$		$x$		$x$

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{\text{HC}_2\text{H}_3\text{O}_2} = 1.8 \times 10^{-5} = \frac{x^2}{(1 \times 10^{-4} - x)}$$

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  $x^2 = 1.8 \times 10^{-9} - 1.8 \times 10^{-5}x$ ; make your math teacher proud and 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  $x = [\text{H}^+] = 3.44 \times 10^{-4}$  and that the  $\text{pH} = -\log(3.44 \times 10^{-4}) = 3.46$  (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. Just draw an arrow through the “ $-x$ ” term and write the word “*neglect*” to communicate that you thought about it, compared it to  $100 K_a$  and decided  $x$  could be *neglected*.

We could not neglect  $x$  in the example we just worked since  $100 K_a$  for acetic acid would equal  $1.8 \times 10^{-3}$  or 0.0018 which is too close to our initial acid concentration of 0.0001.

Need proof? Still not convinced? Sounds too easy? Are we trying to trick you?

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 should you bother to consider sig. figs. 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 solve using the quadratic formula and then I'll solve again by "neglecting x".

### Example

Calculate the pH of a 0.10 M solution of acetic acid. The  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ .

Reaction	$\text{HC}_2\text{H}_3\text{O}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.10		0		0
Change	-x		+x		+x
Equilibrium	$0.10 - x$		x		x

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

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  $x = [\text{H}^+] = 0.0013327$  (way too many sig. figs, I know!)

and that the  $\text{pH} = -\log [0.0013327] = 2.88$  (2 SF)

Had we "neglected x", the math simplifies to

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

*neglect*

and we simply get  $x^2 = 1.8 \times 10^{-6}$

So, take the square root of each side to get

$$\sqrt{x^2} = \sqrt{1.8 \times 10^{-6}}$$
$$x = 0.00134 = [\text{H}^+]$$

$\therefore \text{pH} = -\log [0.001341] = 2.87$  (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! ☺

### Solving Weak Acid Equilibrium Problems

- List the major species in the solution.
- Choose the species that can produce  $\text{H}^+$ , and write balanced equations for the reactions producing  $\text{H}^+$ .
- Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing  $\text{H}^+$ .
- 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  $[\text{HA}]_0 - x \approx [\text{HA}]_0$ .
- Use the 5% rule to verify whether the approximation is valid.
- Calculate  $[\text{H}^+]$  and pH.

#### Exercise 11

#### The pH of Weak Acids

The hypochlorite ion ( $\text{OCl}^-$ ) 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  $\text{Cl}^-$ , for example) and forms the weakly acidic hypochlorous acid ( $\text{HOCl}$ ,  $K_a = 3.5 \times 10^{-8}$ ). 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<sub>2</sub> ( $K_a = 4.0 \times 10^{-4}$ ). Also calculate the concentration of cyanide ion (CN<sup>-</sup>) in this solution at equilibrium.

$$\begin{aligned} \text{pH} &= 1.35 \\ [\text{CN}^-] &= 1.4 \times 10^{-8} \text{ M} \end{aligned}$$

**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<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

b. 0.100 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

$$\begin{aligned} \text{A:} &= 0.42 \% \\ \text{B:} &= 1.3 \% \end{aligned}$$

**Exercise 14****Calculating  $K_a$  from Percent Dissociation**

Lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a  $0.100\text{ M}$  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  $[\text{OH}^-]$  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  $15.0\text{ M}$  solution of  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ).

$$\text{pH} = 12.20$$

## Exercise 16

## The pH of Weak Bases II

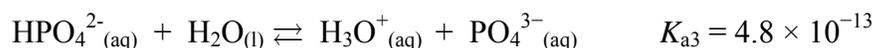
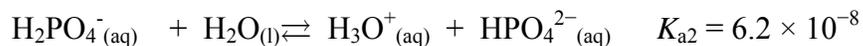
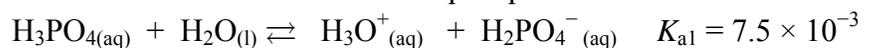
Calculate the pH of a 1.0 M solution of methylamine ( $K_b = 4.38 \times 10^{-4}$ ).

pH = 12.32

### ❖ 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.



- 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	$K_{a1}$	$K_{a2}$	$K_{a3}$
Phosphoric acid	$H_3PO_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.8 \times 10^{-13}$
Arsenic acid	$H_3AsO_4$	$5 \times 10^{-3}$	$8 \times 10^{-8}$	$6 \times 10^{-10}$
Carbonic acid	$H_2CO_3$	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Sulfuric acid	$H_2SO_4$	Large	$1.2 \times 10^{-2}$	
Sulfurous acid	$H_2SO_3$	$1.5 \times 10^{-2}$	$1.0 \times 10^{-7}$	
Hydrosulfuric acid*	$H_2S$	$1.0 \times 10^{-7}$	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	$6.5 \times 10^{-2}$	$6.1 \times 10^{-5}$	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	$7.9 \times 10^{-5}$	$1.6 \times 10^{-12}$	

\*The  $K_{a2}$  value for  $H_2S$  is very uncertain. Because it is so small, the  $K_{a2}$  value is very difficult to measure accurately.

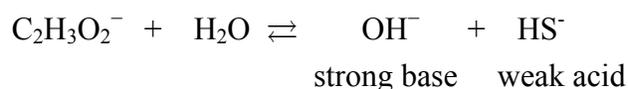


## ❖ ACID-BASE PROPERTIES OF SALTS: HYDROLYSIS (Splitting of water)

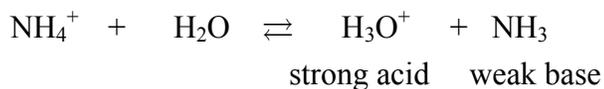
Long ago you learned that salts are produced when an acid and base react in a neutralization reaction. However, salts are **not** always neutral (or soluble for that matter).

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  $\text{NaNO}_3$ . 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.  $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$  should be basic since  $\text{C}_2\text{H}_3\text{O}_2^-$  is the CB of the weak acid  $\text{HC}_2\text{H}_3\text{O}_2$ , while  $\text{K}^+$  does not hydrolyze appreciably.



- **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.  $\text{NH}_4\text{Cl}$  should be weakly acidic, since  $\text{NH}_4^+$  hydrolyzes to give an acidic solution, while  $\text{Cl}^-$  does not hydrolyze.



- 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)

## ACID-BASE PROPERTIES OF SALTS: HYDROLYSIS

Hydrolysis literally means “water splitting”, so *soluble* salts split apart, or hydrolyze, in water. The ions formed may then react with water to form weak acids or bases. Writing hydrolysis reactions is actually quite easy:

### Step 1: Determine *qualitatively* whether the salt is an acidic salt or a basic salt.

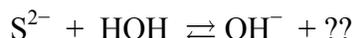
Remember that a salt is the PRODUCT of an acid base reaction. Ask yourself, which acid and which base reacted...were they strong or weak?? Strong wins! The ion that comes from the “strong” is also a “spectator” (It’s a nice alliteration that they both start with an “s”!)

1. A salt such as  $\text{NaNO}_3$  gives a neutral solution—SA & SB
2.  $\text{K}_2\text{S}$  should be weakly *basic* (WA & SB), therefore  $\text{OH}^-$  is a product of the hydrolysis reaction
3.  $\text{FeCl}_2$  should be weakly *acidic* (SA & WB), therefore  $\text{H}^+$  is a product of the hydrolysis reaction

### Step 2: Write the hydrolysis reaction.

Only the ion from the “weak” part of the salt will react with water. Start by writing water as HOH so you can more readily visualize water as being composed of  $\text{H}^+$  and  $\text{OH}^-$ . Let’s reexamine our examples:

1. A salt such as  $\text{NaNO}_3$  gives a neutral solution—SA & SB—the two ions are both from “strong” components, so neither reacts with water.
2.  $\text{K}_2\text{S}$  should be weakly *basic* (WA & SB), therefore  $\text{OH}^-$  is a product of the hydrolysis reaction, so here’s what you can write so far:



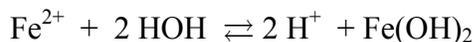
All that is left is to figure out the ?? part! So, if HOH released  $\text{OH}^-$  as one product, then  $\text{H}^+$  reacts with the  $\text{S}^{2-}$  ion to form  $\text{HS}^-$  ion as the other product. Our reaction becomes



3.  $\text{FeCl}_2$  should be weakly *acidic* (SA & WB), therefore  $\text{H}^+$  is a product of the hydrolysis reaction, so here’s what you can write so far:



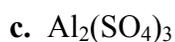
So, if HOH released  $\text{H}^+$  as one product, then  $\text{OH}^-$  reacts with the  $\text{Fe}^{2+}$  ion to form  $\text{Fe}(\text{OH})_2$  as the other product. Our reaction becomes



Once you get the hang of this, you can stop writing water as HOH and substitute  $\text{H}_2\text{O}$  as usual.

**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.

**Exercise 21****Salts as Weak Bases**

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

pH = 8.31

**Exercise 22****Salts as Weak Acids I**

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

pH = 5.13

**Exercise 23****Salts as Weak Acids II**

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

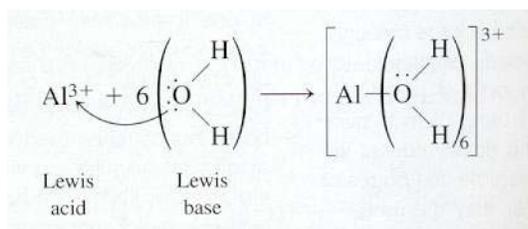
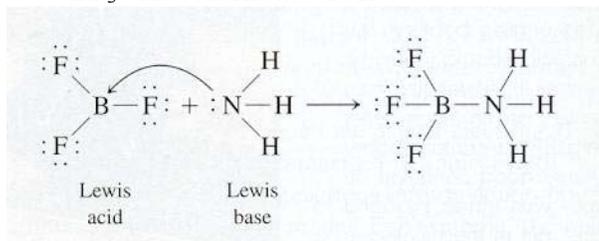
pH = 3.43

**❖ 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!

$\text{BF}_3$ --most famous of all!!

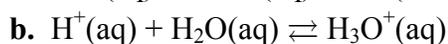
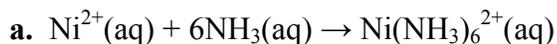
**Exercise 24**

Tell whether each of the following is a Lewis acid or base: Draw structures as proof.

- $\text{PH}_3$
- $\text{BCl}_3$
- $\text{H}_2\text{S}$
- $\text{SF}_4$

**Exercise 25****Lewis Acids and Bases**

For each reaction, identify the Lewis acid and base.



**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  $\text{H}^+$  reacting with  $\text{OH}^-$ .

**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.

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