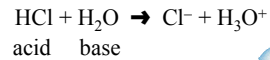# ACIDS and BASES

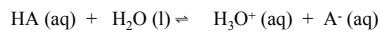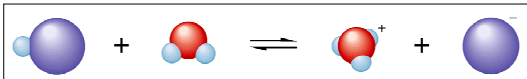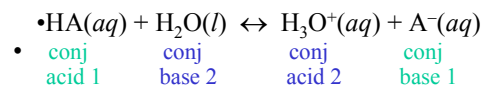## Models of Acids and Bases

• Arrhenius Concept: Acids produce H^+ in solution, bases produce OH^- ion.

• Brønsted-Lowry: Acids are H^+ donors, bases are proton acceptors.

• Review Chapter 4 – Acids & Bases, Section 4.8

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$
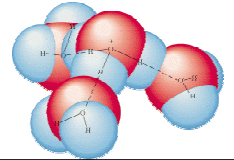
•   acid   base

The reaction of an acid HA with water to form H₃O+ and a conjugate base A-.

HA (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + A⁻ (aq)

Conjugate Acid/Base Pairs

• $HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$

	conj	conj	conj	conj
	acid 1	base 2	acid 2	base 1

• conjugate base: everything that remains of the acid molecule after a proton is lost.

• conjugate acid: formed when the proton is transferred to the base.

Acid Dissociation Constant (K_a)

• $HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$
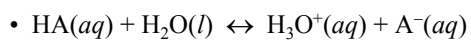
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

Representation of the reaction H₃O⁺ + NH₃.

H_3O^+	NH_3	H_2O	NH_4^+
Acid	Base	Conj. Base	Conj. Acid
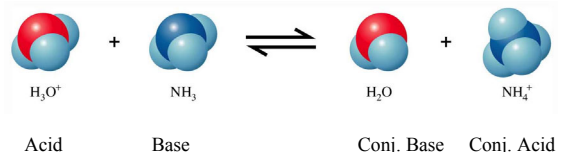
Chemists in the seventeenth century discovered that the substance that gives red ants their irritating bite is an acid with the formula $HCHO_2$. They called this substance formic acid after the ant, whose Latin name is *formica rufus*. Formic acid has the following structural formula and molecular model:

$$
\begin{array}{c}
O \\
\parallel \\
H-C-O-H
\end{array}
$$
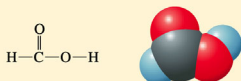
Write the acid–base equilibria connecting all components in the aqueous solution. Now list all of the species present.

$HCOOH$	$+ H_2O$	$\rightleftharpoons$	$HCOO^- +$	H_3O^+
formic acid	water		formate ion	hydronium ion
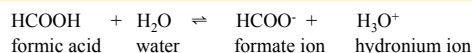
Acid Strength

Strong Acid:

- Its equilibrium position lies far to the right. (HNO_3)
- Yields a weak conjugate base. (NO_3^-)

$$HNO_3\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

$K_a \gg 1$ We do not usually consider the reactants in reactions because the are present in very small amounts!

Table 16.1
Common Strong Acids and Bases

| Strong Acids	Strong Bases*
$HClO_4$	$LiOH$
H_2SO_4	$NaOH$
HI	KOH
HBr	$Ca(OH)_2$
HCl	$Sr(OH)_2$
HNO_3	$Ba(OH)_2$

*In general, the Group IA and Group IIA hydroxides (except beryllium hydroxide) are strong bases.

Acid Strength
(continued)

Weak Acid:

- Its equilibrium lies far to the left. (CH_3COOH)
- Yields a much stronger (it is relatively strong) conjugate base than water. (CH_3COO^-)

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$
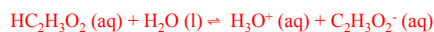
$K_a \ll 1$ Equilibrium favors reactants – but the solution is still acidic – so acetic acid IS an acid!

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}

Increasing acid strength

$$K_a = [H^+][A^-]/[HA]$$

Weak & Strong Acids: (a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.
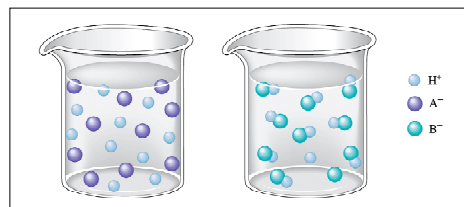

- H^+
- A^-
- B^-

Figure 14.4: Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.
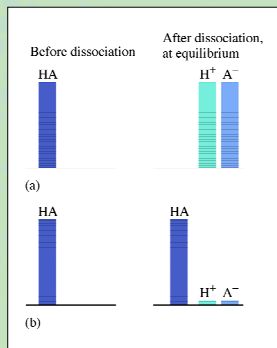
Before dissociation / After dissociation, at equilibrium

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

Bases

• "Strong" and "weak" are used in the same sense for bases as for acids.

• strong = complete dissociation (hydroxide ion supplied to solution)

• $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
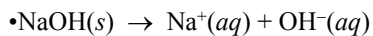
$K_b \gg 1$

Bases
(continued)

• weak = very little dissociation (or reaction with water)

• $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$
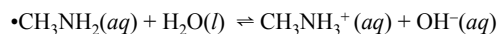
$K_b \ll 1$

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}

$K_b = [OH^-][BH^+]/[B]$

Figure 14.5: The relationship of acid strength and conjugate base strength for the reaction
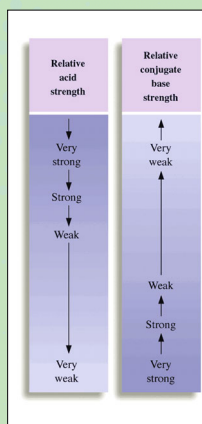
In general, the strength of a weak acid is inversely related to the strength of its conjugate base

Slide 1

Table 16.2
Relative Strengths of Acids and Bases

	Acid	Base	
Strongest acids	$HClO_4$	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$HClO$	ClO^-	
	$HBrO$	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
	HS^-	S^{2-}	
Weakest acids	H_2O	OH^-	Strongest bases

Slide 2

CONCEPT CHECK 16.2

Formic acid, $HCHO_2$, is a stronger acid than acetic acid, $HC_2H_3O_2$. Which is the stronger base, formate ion, CHO_2^-, or acetate ion, $C_2H_3O_2^-$?

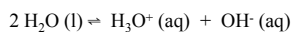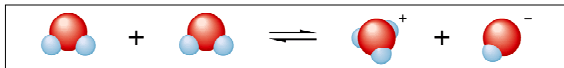Acetic Acid: $K_a = 1.8 \times 10^{-5}$
Formic Acid: $K_a = 1.8 \times 10^{-4}$

Acetate ion: $K_b = 5 \times 10^{-10}$
Formate ion: $K_b = 5 \times 10^{-11}$

Acetate ion!

Slide 3

Figure 14.7: Two water molecules react to form H_3O^+ and OH^-.

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

$[H_3O^+][OH^-] = K_w = 1.01 \times 10^{-14}$

Slide 4

Self-ionization of Water

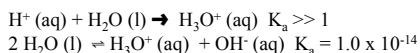- These ions are produced in equal numbers in pure water, so if we let $x = [H^+] = [OH^-]$

$$1.0 \times 10^{-14} = (x)(x) \qquad \text{at } 25\ ^oC$$

$$x = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

- Thus, the concentrations of H^+ and OH^- in pure water are both 1.0×10^{-7} M.
- If you add acid or base to water they are no longer equal but the K_w expression still holds.

Slide 5

Solutions of Strong Acid or Base

- In a solution of a strong acid you can normally ignore the self-ionization of water as a source of $H^+(aq)$.
  - The $H^+(aq)$ concentration is usually determined by the strong acid concentration.
  - However, the self-ionization still exists and is responsible for a small concentration of OH^- ion.

$H^+\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq)\ \ K_a \gg 1$
$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)\ \ K_a = 1.0 \times 10^{-14}$

Slide 6

Solutions of Strong Acid or Base

- As an example, calculate the concentration of OH^- ion in 0.10 M HCl.
  Because you started with 0.10 M HCl (a strong acid) the reaction will produce 0.10 M $H^+(aq)$.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

- Substituting $[H^+] = 0.10$ into the ion-product expression, we get:

$$1.0 \times 10^{-14} = (0.10)[OH^-]$$

Solutions of Strong Acid or Base

- As an example, calculate the concentration of OH⁻ ion in 0.10 M HCl.
  Because you started with 0.10 M HCl (a strong acid) the reaction will produce 0.10 M H⁺(aq).
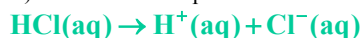
$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

- Substituting [H⁺]=0.10 into the ion-product expression, we get:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} M$$

Solutions of Strong Acid or Base

- Similarly, in a solution of a strong base you can normally ignore the self-ionization of water as a source of OH⁻(aq).
  - The OH⁻(aq) concentration is usually determined by the strong base concentration.
  - However, the self-ionization still exists and is responsible for a small concentration of H⁺ ion.

Solutions of Strong Acid or Base

- As an example, calculate the concentration of H⁺ ion in 0.010 M NaOH.
  Because you started with 0.010 M NaOH (a strong base) the reaction will produce 0.010 M OH⁻(aq).

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

- Substituting [OH⁻]=0.010 into the ion-product expression, we get:

$$1.0 \times 10^{-14} = [H^+](0.010)$$

Solutions of Strong Acid or Base

- As an example, calculate the concentration of H⁺ ion in 0.010 M NaOH.
  Because you started with 0.010 M NaOH (a strong base) the reaction will produce 0.010 M OH⁻(aq).

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

- Substituting [OH⁻]=0.010 into the ion-product expression, we get:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12} M$$

Solutions of Strong Acid or Base

- At 25 ᵒC, you observe the following conditions.

  - In an acidic solution, [H⁺] > 1.0 x 10⁻⁷ M.
  - In a neutral solution, [H⁺] = 1.0 x 10⁻⁷ M.
  - In a basic solution,   [H⁺] < 1.0 x 10⁻⁷ M.

The pH Scale

- pH ≈ −log[H⁺]
- pH in water ranges from 0 to 14.
- $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$
- $pK_w = 14.00 = pH + pOH$
- As pH rises, pOH falls (sum = 14.00).

The pH of a Solution

- For a solution in which the hydrogen-ion concentration is 1.0 x 10⁻³, the pH is:

$$pH = -\log(1.0 \times 10^{-3}) = 3.00$$

- Note that the number of <u>decimal places</u> in the pH equals the number of significant figures in the hydrogen-ion concentration.

The pH of a Solution

- In a **neutral solution**, whose hydrogen-ion concentration is 1.0 x 10⁻⁷, the **pH = 7.00.**
- For **acidic solutions**, the hydrogen-ion concentration is greater than 1.0 x 10⁻⁷, so the **pH is less than 7.00.**
- Similarly, a **basic solution** has a **pH greater than 7.00.**
- Figure 16.6 shows a diagram of the pH scale and the pH values of some common solutions.

Figure 14.8: The pH scale and pH values of some common substances.
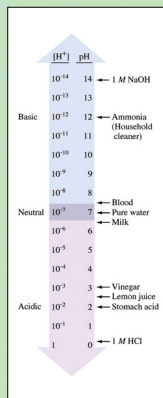
A Problem to Consider

- A sample of orange juice has a hydrogen-ion concentration of 2.9 x 10⁻⁴ M. What is the pH?

$$\mathbf{pH = -\log[H^+]}$$

$$\mathbf{pH = -\log(2.9 \times 10^{-4})}$$

$$\mathbf{pH = 3.54}$$

A Problem to Consider

- The pH of human arterial blood is 7.40. What is the hydrogen-ion concentration?

$$\mathbf{[H^+] = anti\log(-pH)}$$

$$\mathbf{[H^+] = anti\log(-7.40)}$$

$$\mathbf{[H^+] = 10^{-7.40} = 4.0 \times 10^{-8}\,M}$$

The pH of a Solution

- A measurement of the hydroxide ion concentration, similar to pH, is the pOH.
  - The **pOH** of a solution is defined as the negative logarithm of the molar hydroxide-ion concentration.

$$\mathbf{pOH = -\log[OH^-]}$$

The pH of a Solution

- A measurement of the hydroxide ion concentration, similar to pH, is the pOH.
  - Then because $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25 °C, you can show that

$$pH + pOH = 14.00$$

A Problem to Consider

- An ammonia solution has a hydroxide-ion concentration of 1.9×10^{-3} M. What is the pH of the solution?

  You first calculate the pOH:

$$pOH = -\log(1.9 \times 10^{-3}) = 2.72$$

  Then the pH is:

$$pH = 14.00 - 2.72 = 11.28$$

The pH of a Solution

- The pH of a solution can accurately be measured using a pH meter (see Figure 14.9).
  - Although less precise, acid-base indicators are often used to measure pH because they usually change color within a narrow pH range.
  - Figure 16.8 shows the color changes of various acid-base indicators.

Figure 14.9: pH meters are used to measure acidity.

Figure 16.8: Color changes of some acid-based indicators.

Percent Dissociation (Degree of Ionization)

$$\% \text{ dissociation} = \frac{\text{amount dissociated}(M)}{\text{initial concentration}(M)} \times 100\%$$

Weak acids and bases have low values for % dissociation - their degree of ionization is small.

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C.

  $[H^+] = 10^{-3.39} = 0.00041$

- To obtain the degree of dissociation:

$$\text{Degree of dissociation} = \frac{0.00041}{0.012} = 0.034$$

- The percent ionization is obtained by multiplying by 100, which gives 3.4%.

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. Calculate the acid-ionization constant for this acid at 25 °C.

  - It is important to realize that the solution was made 0.012 M in nicotinic acid, however, some molecules ionize making the equilibrium concentration of nicotinic acid less than 0.012 M.

  - We will abbreviate the formula for nicotinic acid as HNic.

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. Calculate the acid-ionization constant for this acid at 25 °C.

  - Let x be the moles per liter of product formed.

$$HNic(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Nic^-(aq)$$

Initial	0.012		0	0
Change	-x		+x	+x
Equilibrium	0.012-x		x	x

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. Calculate the acid-ionization constant for this acid at 25 °C.

  - We can obtain the value of x from the given pH.

$$x = [H_3O^+] = anti\log(-pH)$$
$$x = anti\log(-3.39)$$
$$x = 4.1 \times 10^{-4} = 0.00041$$

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. Calculate the acid-ionization constant for this acid at 25 °C.

  - The equilibrium-constant expression is:

$$K_a = \frac{[H_3O^+][Nic^-]}{[HNic]}$$

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 °C. Calculate the acid-ionization constant for this acid at 25 °C.

  - Substituting the expressions for the equilibrium concentrations, we get

$$K_a = \frac{x^2}{(0.012 - x)}$$

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 ^oC. Calculate the acid-ionization constant for this acid at 25 ^oC.
  - Substitute this value of x in our equilibrium expression.
  - Note first, however, that

$$(0.012 - x) = (0.012 - 0.00041) = 0.01159 \cong 0.012$$

   the concentration of unionized acid remains virtually **unchanged**.

A Problem To Consider

- Nicotinic acid is a weak monoprotic acid with the formula $HC_6H_4NO_2$. A 0.012 M solution of nicotinic acid has a pH of 3.39 at 25 ^oC. Calculate the acid-ionization constant for this acid at 25 ^oC.
  - Substitute this value of x in our equilibrium expression.

$$K_a = \frac{x^2}{(0.012 - x)} \cong \frac{(0.00041)^2}{(0.012)} = 1.4 \times 10^{-5}$$

Solving Weak Acid Equilibrium Problems

- List major species in solution.
- Choose species that can produce H^+ and write reactions.
- Based on K values, decide on dominant equilibrium.
- Write equilibrium expression for dominant equilibrium.
- List initial concentrations in dominant equilibrium.

Solving Weak Acid Equilibrium Problems (continued)

- Define change at equilibrium (as "x").
- Write equilibrium concentrations in terms of x.
- Substitute equilibrium concentrations into equilibrium expression.
- Solve for x the "easy way."
- Verify assumptions using 5% rule.
- Calculate $[H^+]$ and pH.

Calculations With K_a

- If you know the value of K_a, you can calculate the **equilibrium concentrations of species HA, A⁻, and H_3O^+** for solutions of different molarities.

Calculations With K_a

- Note that in our previous example, the degree of dissociation was so small that **"x" was negligible compared to the concentration of nicotinic acid**.
- It is the **small value of the degree of ionization that allowed us to ignore the subtracted x** in the denominator of our equilibrium expression.
- The degree of ionization of a weak acid depends on both the K_a and the concentration of the acid solution.

Calculations With K_a

- **How do you know when you can use this simplifying assumption?**
  - It can be shown that if the acid concentration, C_a, divided by the K_a exceeds 100, that is,

$$\text{if} \quad \frac{C_a}{K_a} > 100$$

  then this simplifying assumption of **ignoring the subtracted x gives an <u>acceptable</u> error of less than 5%.**

Calculations With K_a

- **How do you know when you can use this simplifying assumption?**
  - If the simplifying assumption **is not valid**, you can solve the equilibrium equation exactly by using the **quadratic equation**.

- The next example illustrates this with a solution of aspirin (acetylsalicylic acid), $HC_9H_7O_4$, a common headache remedy.

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and K_a=3.3 x 10⁻⁴ at 25 °C.
  - The molar mass of $HC_9H_7O_4$ is 180.2 g.

    From this we find that the sample contained 0.00180 mol of the acid.

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and K_a=3.3 x 10⁻⁴ at 25 °C.
  - The molar mass of $HC_9H_7O_4$ is 180.2 g.

    Hence, the concentration of the acetylsalicylic acid is 0.00180 mol/0.500 L = **0.0036 M** (Retain two significant figures, the same number of significant figures in K_a).

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and K_a=3.3 x 10⁻⁴ at 25 °C.
  - Note that

$$\frac{C_a}{K_a} = \frac{0.0036}{3.3 \times 10^{-4}} = 11$$

    which is less than 100, so **we must solve the equilibrium equation exactly**.

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and K_a=3.3 x 10⁻⁴ at 25 °C.
  - We will abbreviate the formula for acetylsalicylic acid as **HAcs** and let **x** be the amount of H_3O^+ formed per liter.
  - The amount of acetylsalicylate ion is also **x** mol; the amount of nonionized acetylsalicylic acid is **(0.0036-x) mol**.

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - These data are summarized below.

$$HAcs(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Acs^-(aq)$$

Initial	0.0036		0	0
Change	-x		+x	+x
Equilibrium	0.0036-x		x	x

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - The equilibrium constant expression is

$$\frac{[H_3O^+][Acs^-]}{[HAcs]} = K_a$$

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - If we substitute the equilibrium concentrations and the K_a into the equilibrium constant expression, we get

$$\frac{x^2}{(0.0036 - x)} = 3.3 \times 10^{-4}$$

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - You can solve this equation exactly by using the quadratic formula.
  - Rearranging the preceding equation to put it in the form $ax^2 + bx + c = 0$, we get

$$x^2 + (3.3 \times 10^{-4})x - (1.2 \times 10^{-6}) = 0$$

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - Now substitute into the quadratic formula.

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

A Problem To Consider

- What is the pH at 25 °C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and $K_a=3.3 \times 10^{-4}$ at 25 °C.
  - Now substitute into the quadratic formula.

$$x = \frac{-(3.3 \times 10^{-4}) \pm \sqrt{(3.3 \times 10^{-4})^2 - 4(1.2 \times 10^{-6})}}{2}$$

  - The lower sign in $\pm$ gives a negative root which we can ignore

A Problem To Consider

- What is the pH at 25 ^{o}C of a solution obtained by dissolving 0.325 g of acetylsalicylic acid (aspirin), $HC_9H_7O_4$, in 0.500 L of water? The acid is monoprotic and K_a=3.3 x 10^{-4} at 25 ^{o}C.
  - Taking the upper sign, we get

$$x = [H_3O^+] = 9.4 \times 10^{-4}$$

- Now we can calculate the pH.

$$pH = -\log(9.4 \times 10^{-4}) = 3.03$$

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4 x 10^{-9}.
  - As before, we will follow the three steps in solving an equilibrium.
    1. Write the equation and make a table of concentrations.
    2. Set up the equilibrium constant expression.
    3. Solve for x = [OH⁻].

A Problem To Consider (Weak Base)

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4 x 10^{-9}.
  - Pyridine ionizes by picking up a proton from water (as ammonia does).

$$C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$$

Initial	0.20		0	0
Change	-x		+x	+x
Equilibrium	0.20-x		x	x

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4 x 10^{-9}.
  - Note that

$$\frac{C_a}{K_a} = \frac{0.20}{1.4 \times 10^{-9}} = 1.4 \times 10^8$$

which is much greater than 100, so **we may use the simplifying assumption that (0.20-x) $\cong$ (0.20)**.

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4 x 10^{-9}.
  - The equilibrium expression is

$$\frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = K_b$$

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4 x 10^{-9}.
  - If we substitute the equilibrium concentrations and the K_b into the equilibrium constant expression, we get

$$\frac{x^2}{(0.20 - x)} = 1.4 \times 10^{-9}$$

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4×10^{-9}.
  - Using our simplifying assumption that the x in the denominator is negligible, we get

$$\frac{x^2}{(0.20)} \cong 1.4 \times 10^{-9}$$

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4×10^{-9}.
  - Solving for x we get

$$x^2 \cong (0.20) \times (1.4 \times 10^{-9})$$

$$x = [OH^-] \cong \sqrt{(0.20) \times (1.4 \times 10^{-9})} = 1.7 \times 10^{-5}$$

A Problem To Consider

- What is the pH of a 0.20 M solution of pyridine, C_5H_5N, in aqueous solution? The K_b for pyridine is 1.4×10^{-9}.
  - Solving for pOH

$$pOH = -\log[OH-] = -\log(1.7 \times 10^{-5}) = 4.8$$

  - Since pH + pOH = 14.00

$$pH = 14.00 - pOH = 14.00 - 4.8 = 9.2$$

Polyprotic Acids

- . . . can furnish more than one proton (H^+) to the solution.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (K_{a_1})$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (K_{a_2})$$

Polyprotic Acids

- Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as **polyprotic acids**.
  - Sulfuric acid, for example, can lose two protons in aqueous solution.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$
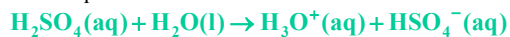
  - The first proton is lost completely followed by a weak ionization of the hydrogen sulfate ion, HSO_4^-.

Polyprotic Acids

- Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as **polyprotic acids**.
  - For a weak diprotic acid like carbonic acid, H_2CO_3, two simultaneous equilibria must be considered.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

Polyprotic Acids

- Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as **polyprotic acids**.
  - Each equilibrium has an associated acid-ionization constant.

    For the loss of the **first** proton

$$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

Polyprotic Acids

- Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as **polyprotic acids**.
  - Each equilibrium has an associated acid-ionization constant.

    For the loss of the **second** proton

$$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.8 \times 10^{-11}$$

Polyprotic Acids

- Some acids have two or more protons (hydrogen ions) to donate in aqueous solution. These are referred to as **polyprotic acids**.
  - The second ionization constant, K_{a2}, for a polyprotic acid is always smaller than the first ionization constant, K_{a1}.
  - In the case of a triprotic acid, such as H_3PO_4, the third ionization constant, K_{a3}, is smaller than the second one, K_{a2}.

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Phosphoric acid	H_3PO_4	7.5×10^{-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}	

Brønsted-Lowry Concept of Acids and Bases

- Some species can act as an acid or a base.
  - An **amphoteric species** is a species that can act either as an acid or a base (it can gain or lose a proton).
  - For example, HCO_3^- acts as a proton donor (an acid) in the presence of OH^-
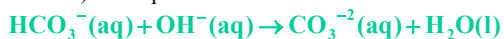
$$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{-2}(aq) + H_2O(l)$$

H^+

Brønsted-Lowry Concept of Acids and Bases

- Some species can act as an acid or a base.
  - An **amphoteric species** is a species that can act either as an acid or a base (it can gain or lose a proton).

    Alternatively, HCO_3 can act as a proton acceptor (a base) in the presence of HF.

$$HCO_3^-(aq) + HF(aq) \rightarrow H_2CO_3(aq) + F^-(aq)$$

H^+

Brønsted-Lowry Concept of Acids and Bases

- The amphoteric characteristic of water is important in the acid-base properties of aqueous solutions.
  - Water can also react as a base with the acid HF.
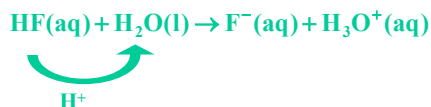
$$HF(aq) + H_2O(l) \rightarrow F^-(aq) + H_3O^+(aq)$$
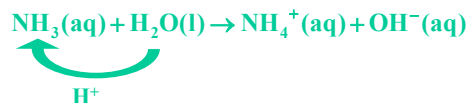
H^+

Brønsted-Lowry Concept of Acids and Bases

- The amphoteric characteristic of water is important in the acid-base properties of aqueous solutions.
  - Water reacts as an acid with the base NH_3.

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$

H^+

Acid-Base Properties of a Salt Solution

- One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.
  - Consider a solution of sodium cyanide, NaCN.

$$NaCN(s) \xrightarrow{H_2O} Na^+(aq) + CN^-(aq)$$

  - A 0.1 M solution has a pH of 11.1 and is therefore fairly basic.

Acid-Base Properties of a Salt Solution

- One of the successes of the Brønsted-Lowry concept of acids and bases was in pointing out that some **ions can act as acids or bases**.
  - Sodium ion, Na^+, is unreactive with water, but the cyanide ion, CN^-, reacts to produce HCN and OH^-.

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

Acid-Base Properties of a Salt Solution

- The **hydrolysis** of an ion is the reaction of an ion with water to produce the **conjugate acid and hydroxide ion** or the **conjugate base and hydronium ion.**
  - The NH_4^+ ion **hydrolyzes** to the conjugate base (NH_3) and hydronium ion.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Predicting Whether a Salt is Acidic, Basic, or Neutral

- These rules apply to normal salts (those in which the anion has no acidic hydrogen)
  1. A salt of a **strong base** and a **strong acid.** The salt has **no hydrolyzable ions** and so gives a **neutral** aqueous solution.

     An example is NaCl.

Predicting Whether a Salt is Acidic, Basic, or Neutral

- These rules apply to normal salts (those in which the anion has no acidic hydrogen)
  2. A salt of a **strong base** and a **weak acid.**

    The anion of the salt is the conjugate of the weak acid. It hydrolyzes to give a **basic** solution.

    An example is NaCN.

Predicting Whether a Salt is Acidic, Basic, or Neutral

- These rules apply to normal salts (those in which the anion has no acidic hydrogen)
  3. A salt of a **weak base** and a **strong acid.**

    The cation of the salt is the conjugate of the weak base. It hydrolyzes to give an **acidic** solution.

    An example is NH_4Cl.

Predicting Whether a Salt is Acidic, Basic, or Neutral

- These rules apply to normal salts (those in which the anion has no acidic hydrogen)
  4. A salt of a **weak base** and a **weak acid.**

    Both ions hydrolyze. You must compare the K_a of the cation with the K_b of the anion.

    If the K_a of the cation is larger the solution is **acidic**.

    If the K_b of the anion is larger, the solution is **basic**.

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)

TABLE 14.6   Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO₃, NaCl, NaNO₃	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	NaC₂H₃O₂, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH₄Cl, NH₄NO₃	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	NH₄C₂H₃O₂, NH₄CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	Al(NO₃)₃, FeCl₃	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

The pH of a Salt Solution

- To calculate the **pH of a salt** solution would require the **K_a of the acidic cation** or the **K_b of the basic anion**. (see Figure 17.8)
  - The ionization constants of ions are not listed directly in tables because the values are easily related to their conjugate species.
  - Thus the **K_b for CN^- is related to the K_a for HCN**.

The pH of a Salt Solution

- To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^-.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \quad K_a$$
$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq) \quad K_b$$
$$\overline{}$$
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w$$

- When these two reactions are added you get the **ionization of water**.

The pH of a Salt Solution

- To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^-.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \quad K_a$$
$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq) \quad K_b$$
$$\overline{}$$
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w$$

- When two reactions are added, their **equilibrium constants are multiplied**.
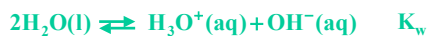

The pH of a Salt Solution

- To see the relationship between K_a and K_b for conjugate acid-base pairs, consider the acid ionization of HCN and the base ionization of CN^-.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \quad K_a$$
$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq) \quad K_b$$
$$\overline{}$$
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w$$

- Therefore,

$$K_a \times K_b = K_w$$

The pH of a Salt Solution

- For a solution of a salt in which **only one ion hydrolyzes**, the calculation of equilibrium composition follows that of weak acids and bases.
  - The only difference is first obtaining the K_a or K_b for the ion that hydrolyzes.
  - The next example illustrates the reasoning and calculations involved.

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C? The K_a for HCN is 4.9 x 10^{-10}.
  - Sodium cyanide gives Na^+ ions and CN^- ions in solution.
  - Only the CN^- ion hydrolyzes.

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 °C? The K_a for HCN is 4.9 x 10^{-10}.
  - The CN^- ion is acting as a base, so first, we must calculate the K_b for CN^-.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

- Now we can proceed with the equilibrium calculation.

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 ^{o}C? The K_a for HCN is 4.9 x 10^{-10}.
  - Let x = [OH$^-$] = [HCN], then substitute into the equilibrium expression.

$$\frac{[\mathbf{HCN}][\mathbf{OH^-}]}{[\mathbf{CN^-}]} = \mathbf{K_b}$$

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 ^{o}C? The K_a for HCN is 4.9 x 10^{-10}.
  - This gives

$$\frac{\mathbf{x^2}}{\mathbf{(0.10 - x)}} = \mathbf{2.0 \times 10^{-5}}$$

A Problem To Consider

- What is the pH of a 0.10 M NaCN solution at 25 ^{o}C? The K_a for HCN is 4.9 x 10^{-10}.
  - Solving the equation, you find that

$$\mathbf{x = [OH^-] = 1.4 \times 10^{-3}}$$

  - Hence,

$$\mathbf{pH = 14.00 - pOH = 14.00 + \log(1.4 \times 10^{-3}) = 11.2}$$

  - As expected, the solution has a pH greater than 7.0.

Structure and Acid-Base Properties

- Two factors for acidity in binary compounds:

    ◈ Bond Polarity (high is good)

    ◈ Bond Strength (low is good)

Molecular Structure and Acid Strength

- Two factors are important in determining the relative acid strengths.
  - One is the polarity of the bond to which the hydrogen atom is attached.
  - The H atom should have a partial positive charge:

$$\overset{\delta+}{\mathbf{H}} - \overset{\delta-}{\mathbf{X}}$$

  - The more polarized the bond, the more easily the proton is removed and the greater the acid strength.

Molecular Structure and Acid Strength

- Two factors are important in determining the relative acid strengths.
  - The second factor is the strength of the bond. Or, in other words, how tightly the proton is held.
  - This depends on the size of atom X.

$$\overset{\delta+}{\mathbf{H}} - \overset{\delta-}{\mathbf{X}}$$

  - The larger atom X, the weaker the bond and the greater the acid strength.

Molecular Structure and Acid Strength

- Consider a series of binary acids from a given column of elements.
  - As you go down the column of elements, the radius increases markedly and the H-X bond strength decreases.
  - You can predict the following order of acidic strength.

HF < HCl < HBr < HI

Molecular Structure and Acid Strength

- As you go across a row of elements, the polarity of the H-X bond becomes the dominant factor.
  - As electronegativity increases going to the right, the polarity of the H-X bond increases and the acid strength increases.
  - You can predict the following order of acidic strength.

$H_3N < H_2O < HF$

Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure: $H - O - Y -$

  - The acidic H atom is always attached to an O atom, which in turn is attached to another atom Y.
  - Bond polarity is the dominant factor in the relative strength of oxoacids.
  - This, in turn, depends on the electronegativity of the atom Y.

Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure: $H - O - Y$

  - If the electronegativity of Y is large, then the O-H bond is relatively polar and the acid strength is greater.

  · We can predict the acid strength for compounds with Y in the same group:

HOCl > HOBr > HOI

Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure:

$$H - O - Y - X$$

  - Other groups, such as O atoms or O-H groups, may be attached to Y.

  - With each additional O atom, Y becomes effectively more electronegative.

Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure:

$$H - O - Y -$$

  - As a result, the H atom becomes more acidic.

  - The acid strengths of the oxoacids of chlorine increase in the following order.

$$HClO < HClO_2 < HClO_3 < HClO_4$$

TABLE 14.8 Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$	H—O—Cl(=O)(—O)—O	Large ($\sim 10^7$)
$HClO_3$	H—O—Cl(=O)—O	~ 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—H)(=O)—O	Large
H_2SO_3	H—O—S(—O—H)—O	1.5×10^{-2}
HNO_3	H—O—N(=O)—O	Large
HNO_2	H—O—N—O	4.0×10^{-4}

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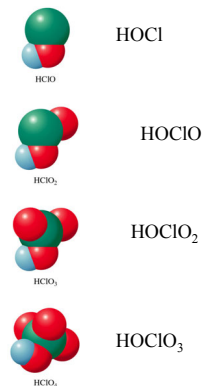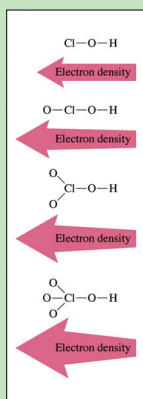Models of HClO, $HClO_2$, $HClO_3$, and $HClO_4$.

HOCl

HOClO

$HOClO_2$

$HOClO_3$

Figure 14.11: The effect of the number of attached oxygens on the O—H bond in a series of chlorine oxyacids.

Cl—O—H
Electron density

O—Cl—O—H
Electron density

O,Cl—O—H
Electron density

O—Cl—O—H
Electron density

Molecular Structure and Acid Strength

- Consider polyprotic acids and their corresponding anions.
  - Each successive H atom becomes more difficult to remove.
  - Therefore the acid strength of a polyprotic acid and its anions decreases with increasing negative charge.

$$HPO_4{}^{2-} < H_2PO_4{}^- < H_3PO_4$$

Oxides

- Acidic Oxides (Acid Anhydrides):
  - O–X bond is strong and covalent.
    - SO_2, NO_2, CrO_3
- Basic Oxides (Basic Anhydrides):
  - O–X bond is ionic.
    - K_2O, CaO

Lewis Acids and Bases

- Lewis Acid: electron pair acceptor
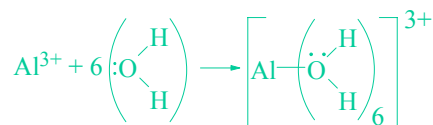- Lewis Base: electron pair donor

$$Al^{3+} + 6 \left(:O \begin{smallmatrix} H \\ \\ H \end{smallmatrix} \right) \longrightarrow \left[Al - \left(\ddot{O} \begin{smallmatrix} H \\ \\ H \end{smallmatrix} \right)_6 \right]^{3+}$$

TABLE 14.10	Three Models for Acids and Bases	
Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

Lewis Concept of Acids and Bases

- The Lewis concept defines an **acid as an electron pair acceptor** and a **base as an electron pair donor.**
  - This concept broadened the scope of acid-base theory to include reactions that did not involve H^+.
  - The Lewis concept embraces many reactions that we might not think of as acid-base reactions.

  Al^{3+} + $6\,H_2O$ ➔ $Al(OH_2)_6{}^{3+}$
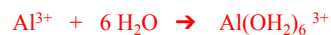
A model of $A(OH_2)_6{}^{3+}$.

A lone pair from the oxygen atom in each water molecule is donated to the Al^{3+} to coordinate covalent bonds between the water molecules and aluminum ion

Al $(OH_2)_6{}^{3+}$