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## *Chapter 15*

### Acids and Bases

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### Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas.

### Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

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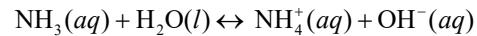
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## Brønsted Acids and Bases

A Brønsted **acid** is a proton donor.

A Brønsted **base** is a proton acceptor.



base      acid       $\leftrightarrow$       acid      base  
base      acid      conjugate acid      conjugate base

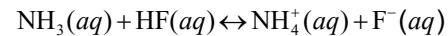
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## Example 15.1<sub>2</sub>

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution.



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## Example 15.1

### Strategy

Remember that a conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid.

### Solution

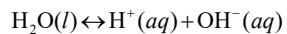
$\text{NH}_3$  has one fewer H atom and one fewer positive charge than  $\text{NH}_4^+$ .  $\text{F}^-$  has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are

- (1)  $\text{NH}_4^+$  and  $\text{NH}_3$  and (2) HF and  $\text{F}^-$ .

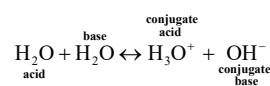
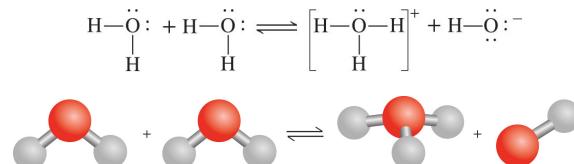
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## Acid-Base Properties of Water



### autoionization of water



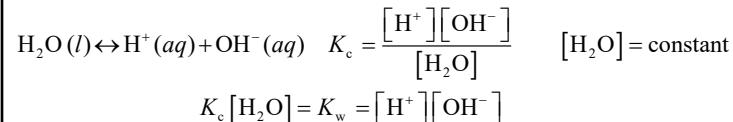
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## The Ion Product of Water



The ***ion-product constant (K<sub>w</sub>)*** is the product of the molar concentrations of H<sup>+</sup> and OH<sup>-</sup> ions **at a particular temperature**.

### Solution Is

At 25°C	$[\text{H}^+] = [\text{OH}^-]$	neutral
$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$	$[\text{H}^+] > [\text{OH}^-]$	acidic
	$[\text{H}^+] < [\text{OH}^-]$	basic

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## Example 15.2

The concentration of OH<sup>-</sup> ions in a certain household ammonia cleaning solution is 0.0025 M. Calculate the concentration of H<sup>+</sup> ions.

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## Example 15.2<sub>2</sub>

### *Strategy*

We are given the concentration of the  $\text{OH}^-$  ions and asked to calculate  $[\text{H}^+]$ . The relationship between  $[\text{H}^+]$  and  $[\text{OH}^-]$  in water or an aqueous solution is given by the ion-product of water,  $K_w$  [Equation (15.3)].

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## Example 15.2<sub>3</sub>

### *Solution*

Rearranging Equation (15.3), we write

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \times 10^{-12} M$$

### *Check*

Because  $[\text{H}^+] < [\text{OH}^-]$  the solution is basic, as we would expect from the earlier discussion of the reaction of ammonia with water.

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## pH – A Measure of Acidity

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

Solution Is At 25°C

**neutral**  $[\text{H}^+] = [\text{OH}^-]$   $[\text{H}^+] = 1.0 \times 1.0^{-7}$  pH = 7

**acidic**  $[\text{H}^+] > [\text{OH}^-]$   $[\text{H}^+] > 1.0 \times 1.0^{-7}$  pH < 7

**basic**  $[\text{H}^+] < [\text{OH}^-]$   $[\text{H}^+] < 1.0 \times 1.0^{-7}$  pH > 7

$$\text{pH} \uparrow [\text{H}^+] \downarrow$$

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## Other Important Relationships

**Table 15.1** The pHs of Some Common Fluids.

Sample	pH Value
Gastric juice in the stomach	1.0-2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8-7.5
Water exposed to air*	5.5
Saliva	6.4-6.9
Milk	6.5
Pure water	7.0
Blood	7.35-7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

\*Water exposed to air for a long period of time absorbs atmospheric CO<sub>2</sub> to form carbonic acid, H<sub>2</sub>CO<sub>3</sub>.

$$\begin{aligned}\text{pOH} &= -\log[\text{OH}^-] \\ [\text{H}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\ -\log[\text{H}^+] - \log[\text{OH}^-] &= 14.00 \\ \text{pH} + \text{pOH} &= 14.00\end{aligned}$$



pH Meter

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### Example 15.3<sub>1</sub>

The concentration of H<sup>+</sup> ions in a bottle of table wine was  $3.2 \times 10^{-4} M$  right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to  $1.0 \times 10^{-3} M$ . Calculate the pH of the wine on these two occasions.

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### Example 15.3<sub>2</sub>

#### *Strategy*

We are given the H<sup>+</sup> ion concentration and asked to calculate the pH of the solution. What is the definition of pH?

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### Example 15.3<sub>3</sub>

*Solution*

According to Equation (15.4),  $\text{pH} = -\log[\text{H}^+]$ .

When the bottle was first opened,  $[\text{H}^+] = 3.2 \times 10^{-4} M$ ,

Which we substitute in Equation (15.4)

$$\begin{aligned}\text{pH} &= -\log[\text{H}^+] \\ &= -\log(3.2 \times 10^{-4}) = 3.49\end{aligned}$$

On the second occasion,  $[\text{H}^+] = 1.0 \times 10^{-3} M$ , so that

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

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### Example 15.3<sub>4</sub>

*Comment*

The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

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### Example 15.4<sub>1</sub>

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the  $\text{H}^+$  ion concentration of the rainwater.

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### Example 15.4<sub>2</sub>

#### *Strategy*

Here we are given the pH of a solution and asked to calculate  $[\text{H}^+]$ .

Because pH is defined as  $\text{pH} = -\log[\text{H}^+]$ , we can solve for  $[\text{H}^+]$  by taking the antilog of the pH; that is,  $[\text{H}^+] = 10^{-\text{pH}}$ , as shown in Equation (15.5).

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### Example 15.4<sub>3</sub>

*Solution*

From Equation (15.4)

$$\text{pH} = -\log[H^+] = 4.82$$

Therefore,

$$\log[H^+] = -4.82$$

To calculate  $[H^+]$ , We need to take the antilog of  $-4.82$

$$[H^+] = 10^{-4.82} = 1.5 \times 10^{-5} M$$

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### Example 15.4<sub>4</sub>

*Check*

Because the pH is between 4 and 5, we can expect  $[H^+]$  to be between  $1 \times 10^{-4} M$  and  $1 \times 10^{-5} M$ .

Therefore, the answer is reasonable.

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### Example 15.5<sub>1</sub>

In a NaOH solution  $[\text{OH}^-]$  is  $2.9 \times 10^{-4} M$ .

Calculate the pH of the solution.

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### Example 15.5<sub>2</sub>

#### *Strategy*

Solving this problem takes two steps. First, we need to calculate pOH using Equation (15.7). Next, we use Equation (15.9) to calculate the pH of the solution.

#### *Solution*

We use Equation (15.7):

$$\begin{aligned}\text{pOH} &= -\log [\text{OH}^-] \\ &= -\log (2.9 \times 10^{-4}) \\ &= 3.54\end{aligned}$$

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### Example 15.5 <sub>3</sub>

Now we use Equation (15.9):

$$\begin{aligned} \text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 3.54 = \mathbf{10.46} \end{aligned}$$

Alternatively, we can use the ion-product constant of water,  
 $K_w = [\text{H}^+][\text{OH}^-]$  to calculate  $[\text{H}^+]$ ,  
and then we can calculate the pH from the  $[\text{H}^+]$

**Check**

The answer shows that the solution is basic ( $\text{pH} > 7$ ), which is consistent with a NaOH solution.

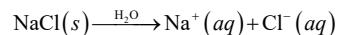
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### Electrolytes <sub>1</sub>

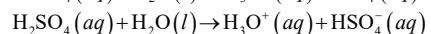
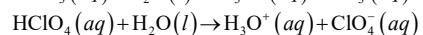
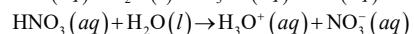
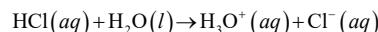
Strong Electrolyte – 100% dissociation



Weak Electrolyte – not completely dissociated



**Strong Acids** are strong electrolytes



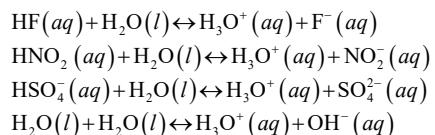
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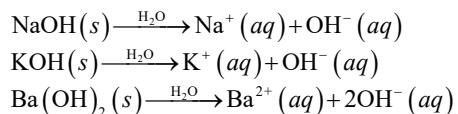
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## Electrolytes <sub>2</sub>

**Weak Acids** are weak electrolytes



**Strong Bases** are strong electrolytes



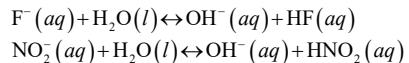
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## Electrolytes <sub>3</sub>

**Weak Bases** are weak electrolytes



**Conjugate acid-base pairs:**

The conjugate base of a strong acid has no measurable strength.

$\text{H}_3\text{O}^+$  is the strongest acid that can exist in aqueous solution.

The  $\text{OH}^-$  ion is the strongest base that can exist in aqueous solution.

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## Acids and Conjugate Bases

**Table 15.2** Relative Strengths of Conjugate Acid-Base Pairs

Acid	Conjugate Base
Strong acids	ClO <sub>4</sub> <sup>-</sup> (perchlorate ion)
HI (hydroiodic acid)	I <sup>-</sup> (iodide ion)
HBr (hydrobromic acid)	Br <sup>-</sup> (bromide ion)
HCl (hydrochloric acid)	Cl <sup>-</sup> (chloride ion)
H <sub>2</sub> SO <sub>4</sub> (sulfuric acid)	HSO <sub>4</sub> <sup>-</sup> (hydrogen sulfate ion)
HNO <sub>3</sub> (nitric acid)	NO <sub>3</sub> <sup>-</sup> (nitrate ion)
H <sub>3</sub> O <sup>+</sup> (hydronium ion)	H <sub>2</sub> O (water)
HSO <sub>4</sub> <sup>-</sup> (hydrogen sulfate ion)	SO <sub>4</sub> <sup>2-</sup> (sulfate ion)
HF (hydrofluoric acid)	F <sup>-</sup> (fluoride ion)
HNO <sub>2</sub> (nitrous acid)	NO <sub>2</sub> <sup>-</sup> (nitrite ion)
HCOOH (formic acid)	HCOO <sup>-</sup> (formate ion)
CH <sub>3</sub> COOH (acetic acid)	CH <sub>3</sub> COO <sup>-</sup> (acetate ion)
NH <sub>4</sub> <sup>+</sup> (ammonium ion)	NH <sub>3</sub> (ammonia)
HCN (hydrocyanic acid)	CN <sup>-</sup> (cyanide ion)
H <sub>2</sub> O (water)	OH <sup>-</sup> (hydroxide ion)
NH <sub>3</sub> (ammonia)	NH <sub>2</sub> <sup>-</sup> (amide ion)

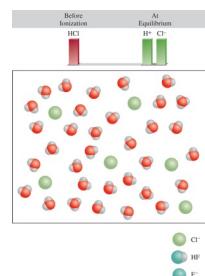
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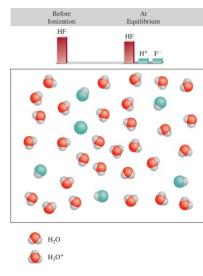
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## Strong vs. Weak Acids

Strong Acid (HCl)



Weak Acid (HF)



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### Example 15.6<sub>1</sub>

Calculate the pH of a

(a)  $1.0 \times 10^{-3} M$  HCl solution

(b) 0.020 M Ba(OH)<sub>2</sub> solution

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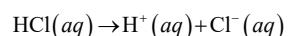
### Example 15.6<sub>2</sub>

#### *Strategy*

Keep in mind that HCl is a strong acid and Ba(OH)<sub>2</sub> is a strong base. Thus, these species are completely ionized and no HCl or Ba(OH)<sub>2</sub> will be left in solution.

#### *Solution*

a) The ionization of HCl is



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### Example 15.6<sub>3</sub>

The concentrations of all the species (HCl, H<sup>+</sup>, and Cl<sup>-</sup>) before and after ionization can be represented as follows:

$\text{HCl}(aq) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$
Initial ( <i>M</i> ): $1.0 \times 10^{-3}$ 0.0      0.0
Change ( <i>M</i> ): $-1.0 \times 10^{-3}$ $+1.0 \times 10^{-3}$ $+1.0 \times 10^{-3}$
Final ( <i>M</i> )      0.0 $1.0 \times 10^{-3}$ $1.0 \times 10^{-3}$

A positive (+) change represents an increase and a negative (-) change indicates a decrease in concentration. Thus,

$$\begin{aligned} [\text{H}^+] &= 1.0 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log(1.0 \times 10^{-3}) \\ &= \mathbf{3.00} \end{aligned}$$

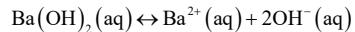
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### Example 15.6<sub>4</sub>

- (b) Ba(OH)<sub>2</sub> is a strong base; each Ba(OH)<sub>2</sub> unit produces two OH<sup>-</sup> ions:



The changes in the concentrations of all the species can be represented as follows:

$\text{Ba(OH)}_2(aq) \rightarrow \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq)$
Initial ( <i>M</i> ):      0.020      0.00      0.00
Change ( <i>M</i> ):      -0.020      +0.020      +2(0.020)
Final ( <i>M</i> )      0.00      0.020      0.040

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### Example 15.6<sub>5</sub>

Thus,

$$\begin{aligned} [\text{OH}^-] &= 0.040 \text{ M} \\ \text{pOH} &= -\log(0.040) = 1.40 \end{aligned}$$

Therefore, from Equation (15.8),

$$\begin{aligned} \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 1.40 \\ &= \mathbf{12.60} \end{aligned}$$

**Check**

Note that in both (a) and (b) we have neglected the contribution of the autoionization of water to  $[\text{H}^+]$  and  $[\text{OH}^-]$  because  $1.0 \times 10^{-7} \text{ M}$  is so small compared with  $1.0 \times 10^{-3}$  and  $0.040 \text{ M}$ .

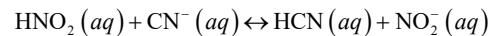
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### Example 15.7<sub>1</sub>

Predict the direction of the following reaction in aqueous solution:



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## Example 15.7<sub>2</sub>

### *Strategy*

The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO<sub>2</sub><sup>-</sup>, or to the left, favoring HNO<sub>2</sub> and CN<sup>-</sup>. Which of the two is a stronger acid and hence a stronger proton donor: HNO<sub>2</sub> or HCN? Which of the two is a stronger base and hence a stronger proton acceptor: CN<sup>-</sup> or NO<sub>2</sub><sup>-</sup>?

Remember that the stronger the acid, the weaker its conjugate base.

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## Example 15.7<sub>3</sub>

### *Solution*

In Table 15.2 we see that HNO<sub>2</sub> is a stronger acid than HCN. Thus, CN<sup>-</sup> is a stronger base than NO<sub>2</sub><sup>-</sup>.

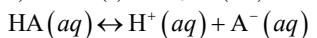
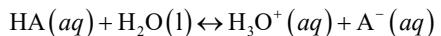
The net reaction will proceed from left to right as written because HNO<sub>2</sub> is a better proton donor than HCN (and CN<sup>-</sup> is a better proton acceptor than NO<sub>2</sub><sup>-</sup>).

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## Weak Acids (HA) and Acid Ionization Constants



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

$K_a$  is the **acid ionization constant**

$K_a \uparrow$       weak acid strength  $\uparrow$

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## Ionization Constants of Some Weak Acids 1

**Table 15.3** Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	$K_a$	Conjugate Base	$K_b$ *
Hydrofluoric acid	HF	H—F	$7.1 \times 10^{-4}$	$\text{F}^-$	$1.4 \times 10^{-11}$
Nitrous acid	$\text{HNO}_2$	$\text{O}=\text{N}—\text{O}—\text{H}$	$4.5 \times 10^{-4}$	$\text{NO}_2^-$	$2.2 \times 10^{-11}$
Acetylsalicylic acid (aspirin)	$\text{C}_9\text{H}_8\text{O}_4$		$3.0 \times 10^{-4}$	$\text{C}_9\text{H}_8\text{O}_4^-$	$3.3 \times 10^{-11}$
Formic acid	$\text{HCOOH}$		$1.7 \times 10^{-4}$	$\text{HCOO}^-$	$5.9 \times 10^{-11}$
Ascorbic acid*	$\text{C}_6\text{H}_8\text{O}_6$		$8.0 \times 10^{-5}$	$\text{C}_6\text{H}_8\text{O}_6^-$	$1.3 \times 10^{-10}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$		$6.5 \times 10^{-5}$	$\text{C}_6\text{H}_5\text{COO}^-$	$1.5 \times 10^{-10}$
Acetic acid	$\text{CH}_3\text{COOH}$		$1.8 \times 10^{-5}$	$\text{CH}_3\text{COO}^-$	$5.6 \times 10^{-10}$
Hydrocyanic acid	HCN		$4.9 \times 10^{-10}$	$\text{CN}^-$	$2.0 \times 10^{-5}$
Phenol	$\text{C}_6\text{H}_5\text{OH}$		$1.3 \times 10^{-10}$	$\text{C}_6\text{H}_5\text{O}^-$	$7.7 \times 10^{-5}$

\*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.

The base ionization constant  $K_b$  is discussed in Section 15.6.

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## Ionization Constants of Some Weak Acids 2

Solving weak acid ionization problems:

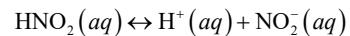
1. Identify the major species that can affect the pH. In most cases, you can ignore the autoionization of water. Ignore  $[\text{OH}^-]$  because it is determined by  $[\text{H}^+]$ .
2. Use ICE to express the equilibrium concentrations in terms of single unknown  $x$ .
3. Write  $K_a$  in terms of equilibrium concentrations. Solve for  $x$  by the approximation method. If approximation is not valid, solve for  $x$  exactly.
4. Calculate concentrations of all species and/or pH of the solution.

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## Example 15.8 1

Calculate the pH of a 0.036 M nitrous acid ( $\text{HNO}_2$ ) solution:

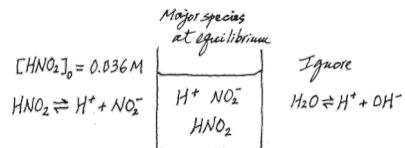

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## Example 15.8<sub>2</sub>

### Strategy

Recall that a weak acid only partially ionizes in water. We are given the initial concentration of a weak acid and asked to calculate the pH of the solution at equilibrium. It is helpful to make a sketch to keep track of the pertinent species.



As in Example 15.6, we ignore the ionization of  $\text{H}_2\text{O}$  so the major source of  $\text{H}^+$  ions is the acid. The concentration of  $\text{OH}^-$  ions is very small as we would expect from an acidic solution so it is present as a minor species.

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## Example 15.8<sub>4</sub>

### Solution

We follow the procedure already outlined.

**Step 1:** The species that can affect the pH of the solution are  $\text{HNO}_2$ ,  $\text{H}^+$ , and the conjugate base  $\text{NO}_2^-$ . We ignore water's contribution to  $[\text{H}^+]$ .

**Step 2:** Letting  $x$  be the equilibrium concentration of  $\text{H}^+$  and  $\text{NO}_2^-$  ions in mol/L, we summarize:

$\text{HNO}_2(aq) \leftrightarrow \text{H}^+(aq) + \text{NO}_2^-(aq)$			
Initial (M):	0.036	0.00	0.00
Change (M):	- $x$	+ $x$	+ $x$
Equilibrium (M):	0.036 - $x$	$x$	$x$

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### Example 15.8<sub>3</sub>

*Step 3:* From Table 15.3 we write

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x}$$

Applying the approximation  $0.036 - x \approx 0.036$ , we obtain

$$4.5 \times 10^{-4} = \frac{x^2}{0.36 - x} \approx \frac{x^2}{0.036}$$

$$x^2 = 1.62 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3} M$$

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### Example 15.8<sub>5</sub>

To test the approximation,

$$\frac{4.0 \times 10^{-3} M}{0.036 M} \times 100\% = 11\%$$

Because this is greater than 5%, our approximation is not valid and we must solve the quadratic equation, as follows:

$$x^2 + 4.5 \times 10^{-4} x - 1.62 \times 10^{-5} = 0$$

$$x = \frac{-4.5 \times 10^{-4} \pm \sqrt{(4.5 \times 10^{-4})^2 - 4(1)(-1.62 \times 10^{-5})}}{2(1)}$$

$$= 3.8 \times 10^{-3} M \text{ or } -4.3 \times 10^{-3} M$$

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### Example 15.8<sub>6</sub>

The second solution is physically impossible, because the concentration of ions produced as a result of ionization cannot be negative. Therefore, the solution is given by the positive root,  $x = 3.8 \times 10^{-3} M$ .

*Step 4:* At equilibrium

$$\begin{aligned} [\text{H}^+] &= 3.8 \times 10^{-3} M \\ \text{pH} &= -\log(3.8 \times 10^{-3}) \\ &= 2.42 \end{aligned}$$

**Check**

Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. Compare the calculated pH with that of a 0.036 M strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.

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### Example 15.9<sub>1</sub>

The pH of a 0.10 M solution of formic acid (HCOOH) is 2.39. What is the  $K_a$  of the acid?

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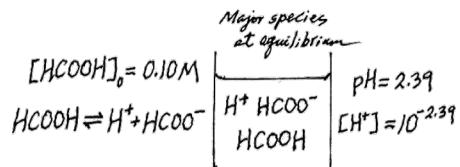
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## Example 15.9<sub>2</sub>

### Strategy

Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate  $K_a$ , then, we need to know the concentrations of all three species:  $[H^+]$ ,  $[HCOO^-]$ , and  $[HCOOH]$  at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



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## Example 15.9<sub>3</sub>

### Solution

We proceed as follows.

*Step 1:* The major species in solution are HCOOH,  $H^+$ , and the conjugate base  $HCOO^-$ .

*Step 2:* First we need to calculate the hydrogen ion concentration from the pH value

$$\begin{aligned} \text{pH} &= -\log[H^+] \\ 2.39 &= -\log[H^+] \end{aligned}$$

Taking the antilog of both sides, we get

$$[H^+] = 10^{-2.39} = 4.1 \times 10^{-3} M$$

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### Example 15.9<sub>4</sub>

Next we summarize the changes:

$\text{HCOOH} \text{ (aq)} \leftrightarrow \text{H}^+ \text{ (aq)} + \text{HCOO}^- \text{ (aq)}$
Initial ( $M$ ):      0.10      0.00      0.00
Change ( $M$ ): $-4.1 \times 10^{-3}$ $+4.1 \times 10^{-3}$ $+4.1 \times 10^{-3}$
Equilibrium ( $M$ ): $(0.10 - 4.1 \times 10^{-3})$ $4.1 \times 10^{-3}$ $4.1 \times 10^{-3}$

Note that because the pH and hence the  $\text{H}^+$  ion concentration is known, it follows that we also know the concentrations of  $\text{HCOOH}$  and  $\text{HCOO}^-$  at equilibrium.

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### Example 15.9<sub>5</sub>

*Step 3:* The ionization constant of formic acid is given by

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \\ &= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})} \\ &= 1.8 \times 10^{-4} \end{aligned}$$

**Check**

The  $K_a$  value differs slightly from the one listed in Table 15.3 because of the rounding-off procedure we used in the calculation.

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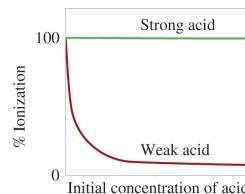
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## Percent Ionization

$$\text{percent ionization} = \frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acids}} \times 100\%$$

For a monoprotic acid HA,

$$\text{Percent Ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\% \quad [\text{HA}]_0 = \text{initial concentration}$$



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## Weak Bases and Base Ionization Constants



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$K_b$  is the **base ionization constant**

$K_b \uparrow$  weak base strength  $\uparrow$

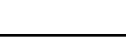
Solve weak base problems like weak acids *except* solve for  $[\text{OH}^-]$  instead of  $[\text{H}^+]$ .

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## Ionization Constants of Some Weak Bases

**Table 15.4** Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

Name of Base	Formula	Structure	$K_b^*$	Conjugate Acid	$K_a$
Ethylamine	$C_2H_5NH_2$		$5.6 \times 10^{-4}$	$C_2H_5\bar{N}H_3$	$1.8 \times 10^{-11}$
Methylamine	$CH_3NH_2$		$4.4 \times 10^{-4}$	$CH_3\bar{N}H_3$	$2.3 \times 10^{-11}$
Ammonia	$NH_3$		$1.8 \times 10^{-5}$	$NH_4^+$	$5.6 \times 10^{-10}$
Pyridine	$C_6H_5N$		$1.7 \times 10^{-9}$	$C_6H_5\bar{N}H$	$5.9 \times 10^{-6}$
Aniline	$C_6H_5NH_2$		$3.8 \times 10^{-9}$	$C_6H_5\bar{N}H_3$	$2.6 \times 10^{-5}$
Caffeine	$C_8H_{10}N_4O_2$		$5.3 \times 10^{-14}$	$C_8H_{10}\bar{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$		$1.5 \times 10^{-14}$	$H_2NC\bar{O}NH_3$	0.67

\*The nitrogen atom with the lone pair accounts for each compound's basicity. In the case of urea,  $K_b$  can be associated with either nitrogen atom.

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### Example 15.10

What is the pH of a 0.40 M ammonia solution?

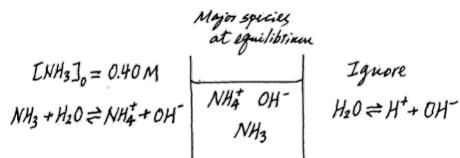
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## Example 15.10<sub>2</sub>

### Strategy

The procedure here is similar to the one used for a weak acid (see Example 15.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and OH<sup>-</sup>. The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:



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## Example 15.10<sub>3</sub>

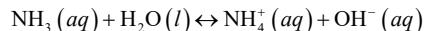
### Solution

We proceed according to the following steps.

*Step 1:* The major species in an ammonia solution are NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and OH<sup>-</sup>.

We ignore the very small contribution to OH<sup>-</sup> concentration by water.

*Step 2:* Letting x be the equilibrium concentration of NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions in mol/L, we summarize:



Initial (M):	0.40	0.00	0.00
Change (M):	-x	+x	+x
Equilibrium (M):	0.40 - x	x	x

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### Example 15.10<sub>4</sub>

*Step 3:* Table 15.4 gives us  $K_b$ :

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

Applying the approximation  $0.040 - x \approx 0.040$ , we obtain

$$\begin{aligned} 1.8 \times 10^{-5} &= \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40} \\ x^2 &= 7.2 \times 10^{-6} \\ x &= 2.7 \times 10^{-3} M \end{aligned}$$

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### Example 15.10<sub>5</sub>

To test the approximation, we write

$$\frac{2.7 \times 10^{-3} M}{0.40 M} \times 100\% = 0.68\%$$

Therefore, the approximation is valid.

*Step 4:* At equilibrium,  $[\text{OH}^-] = 2.7 \times 10^{-3} M$ . Thus,

$$\begin{aligned} \text{pOH} &= -\log(2.7 \times 10^{-3}) \\ &= 2.57 \\ \text{pH} &= 14.00 - 2.75 \\ &= 11.43 \end{aligned}$$

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### Example 15.10<sub>6</sub>

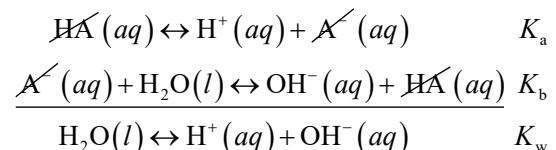
*Check*

Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a 0.40 M strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

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### Ionization Constants of Conjugate Acid-Base Pairs



$$K_a K_b = K_w$$

Weak Acid and Its Conjugate Base

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

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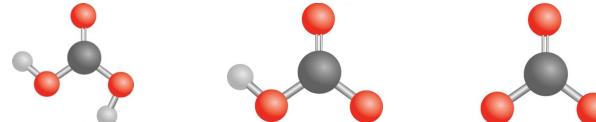
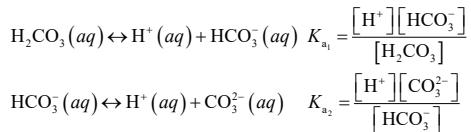
## Diprotic and Triprotic Acids

May yield more than one hydrogen ion per molecule.

Ionize in a stepwise manner; that is, they lose one proton at a time.

An ionization constant expression can be written for each ionization stage.

Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution.



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## Ionization Constants of Some Polyprotic Acids

Name of Acid	Formula	Structure	$K_a$	Conjugate Base	$K_b$
Sulfuric acid	$\text{H}_2\text{SO}_4$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{O}-\text{H}$	very large	$\text{HSO}_4^-$	very small
Hydrogen sulfide ion	$\text{HSO}_4^-$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{O}^-$	$1.3 \times 10^{-1}$	$\text{SO}_4^{2-}$	$7.7 \times 10^{-13}$
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{H}$	$6.2 \times 10^{-1}$	$\text{HC}_2\text{O}_4^-$	$1.5 \times 10^{-13}$
Hydrogen oxalate ion	$\text{HC}_2\text{O}_4^-$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-$	$6.1 \times 10^{-1}$	$\text{C}_2\text{O}_4^{2-}$	$1.6 \times 10^{-13}$
Sulfurous acid	$\text{H}_2\text{SO}_3$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{O}-\text{H}$	$1.3 \times 10^{-1}$	$\text{HSO}_3^-$	$7.7 \times 10^{-13}$
Hydrogen sulfite ion	$\text{HSO}_3^-$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{O}^-$	$6.3 \times 10^{-1}$	$\text{SO}_3^{2-}$	$1.6 \times 10^{-13}$
Citric acid	$\text{H}_3\text{C}_6\text{O}_7$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{H}$	$4.2 \times 10^{-1}$	$\text{H}_2\text{C}_6\text{O}_6$	$2.4 \times 10^{-4}$
Hydrogen citrate ion	$\text{H}_2\text{C}_6\text{O}_6$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{C}(\text{H})-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-$	$4.8 \times 10^{-1}$	$\text{C}_6\text{O}_5^-$	$2.1 \times 10^{-4}$
Phosphoric acid	$\text{H}_3\text{PO}_4$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{P}(\text{O})(\text{H})-\text{O}-\text{H}$	$7.5 \times 10^{-3}$	$\text{H}_2\text{PO}_4^-$	$1.3 \times 10^{-12}$
Hydrogen phosphate ion	$\text{H}_2\text{PO}_4^-$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{P}(\text{O})(\text{H})-\text{O}^-$	$1.8 \times 10^{-3}$	$\text{HPO}_4^{2-}$	$1.6 \times 10^{-13}$
Phosphate acid	$\text{H}_3\text{PO}_3$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{P}(\text{O})(\text{H})-\text{O}-\text{H}$	$7.3 \times 10^{-1}$	$\text{H}_2\text{PO}_3^-$	$1.3 \times 10^{-13}$
Dihydrogen phosphate ion	$\text{H}_2\text{PO}_3^-$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{P}(\text{O})(\text{H})-\text{O}^-$	$6.2 \times 10^{-4}$	$\text{HPO}_3^{2-}$	$1.6 \times 10^{-13}$
Hydrogen phosphite ion	$\text{HPO}_3^{2-}$	$\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{H})-\text{P}(\text{O})(\text{H})-\text{O}^-$	$4.8 \times 10^{-5}$	$\text{PO}_3^{3-}$	$2.1 \times 10^{-13}$

$\text{H}_2\text{O}$  has water dissociation and reacts to any extent conceivable to give solution of  $\text{H}_3\text{O}^+$ . But  $K_a$  value here refers to the process  $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HO}^-$ .

The ionization constant of  $\text{H}_2\text{O}$  is  $1.8 \times 10^{-16}$  and  $\text{K}_b = 5.5 \times 10^{-15}$ .

The value listed here is only an estimate.

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### Example 15.11<sub>1</sub>

Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is a poisonous substance used chiefly as a bleaching and cleansing agent (for example, to remove bathtub rings). Calculate the concentrations of all the species present at equilibrium in a 0.10 M solution.

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### Example 15.11<sub>2</sub>

#### *Strategy*

Determining the equilibrium concentrations of the species of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. We follow the same procedure as that used for a monoprotic acid for each stage, as in Example 15.8. Note that the conjugate base from the first stage of ionization becomes the acid for the second stage ionization.

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### Example 15.11 <sub>3</sub>

**Solution**

We proceed according to the following steps.

**Step 1:** The major species in solution at this stage are the nonionized acid, H<sup>+</sup> ions, and the conjugate base, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>.

**Step 2:** Letting x be the equilibrium concentration of H<sup>+</sup> and HC<sub>2</sub>O<sub>4</sub><sup>-</sup> ions in mol/L, we summarize:

$\text{H}_2\text{C}_2\text{O}_4(aq) \leftrightarrow \text{H}^+(aq) + \text{HC}_2\text{O}_4^-(aq)$
Initial (M):
Change (M):
Equilibrium (M):

Initial (M):      0.10      0.00      0.00  
 Change (M):      -x      +x      +x  
 Equilibrium (M):      0.10 - x      x      x

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### Example 15.11 <sub>4</sub>

**Step 3:** Table 15.5 gives us

$$K_a = \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

Applying the approximation  $0.10 - x \approx 0.10$ , we obtain

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x^2 = 6.5 \times 10^{-3}$$

$$x = 8.1 \times 10^{-2} \text{ M}$$

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### Example 15.11<sub>5</sub>

To test the approximation,

$$\frac{8.1 \times 10^{-2} M}{0.10 M} \times 100\% = 81\%$$

Clearly the approximation is not valid. Therefore, we must solve the quadratic equation

$$x^2 + 6.5 \times 10^{-2} x - 6.5 \times 10^{-3} = 0$$

The result is  $x = 0.054 M$ .

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### Example 15.11<sub>6</sub>

*Step 4:* When the equilibrium for the first stage of ionization is reached, the concentrations are

$$[\text{H}^+] = 0.054 M$$

$$[\text{HC}_2\text{O}_4^-] = 0.054 M$$

$$[\text{H}_2\text{C}_2\text{O}_4] = (0.10 - 0.054) M = 0.046 M$$

Next we consider the second stage of ionization.

*Step 1:* At this stage, the major species are  $\text{HC}_2\text{O}_4^-$ , which acts as the acid in the second stage of ionization,  $\text{H}^+$  and the conjugate base  $\text{C}_2\text{O}_4^{2-}$ .

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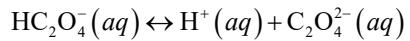
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### Example 15.11 <sub>7</sub>

*Step 2:* Letting  $y$  be the equilibrium concentration of  $\text{H}^+$  and

$\text{C}_2\text{O}_4^{2-}$  ions in mol/L, we summarize:



Initial ( $M$ ):	0.054	0.054	0.00
Change ( $M$ ):	- $y$	+ $y$	+ $y$
Equilibrium ( $M$ ):	0.054 - $y$	0.054 + $y$	$y$

*Step 3:* Table 15.5 gives us

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{(0.054 - y)}$$

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### Example 15.11 <sub>8</sub>

Applying the approximation  $0.054 + y \approx 0.054$  and  $0.054 - y \approx 0.054$ , we obtain

$$\frac{(0.054)(y)}{(0.054)} = y = 6.1 \times 10^{-5} M$$

and we test the approximation,

$$\frac{6.1 \times 10^{-5} M}{0.054 M} \times 100\% = 0.11\%$$

The approximation is valid.

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### Example 15.11 ,

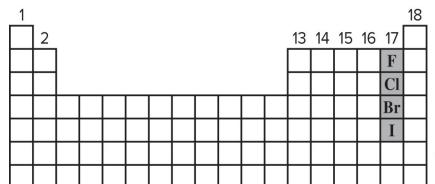
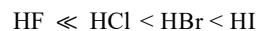
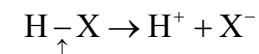
*Step 4:* At equilibrium,

$$\begin{aligned} [\text{H}_2\text{C}_2\text{O}_4] &= \mathbf{0.046 \text{ M}} \\ \left[\text{HC}_2\text{O}_4^-\right] &= (0.054 - 6.1 \times 10^{-5}) \text{ M} = \mathbf{0.054 \text{ M}} \\ \left[\text{H}^+\right] &= (0.054 + 6.1 \times 10^{-5}) \text{ M} = \mathbf{0.054 \text{ M}} \\ \left[\text{C}_2\text{O}_4^{2-}\right] &= \mathbf{6.1 \times 10^{-5} \text{ M}} \\ \left[\text{OH}^-\right] &= 1.0 \times 10^{-14} / 0.054 = \mathbf{1.9 \times 10^{-13} \text{ M}} \end{aligned}$$

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## Molecular Structure and Acid Strength



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## Bond Enthalpies for Hydrogen Halides

**Table 15.6** Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids

Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

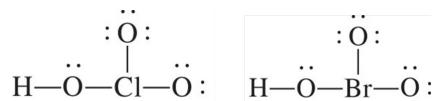
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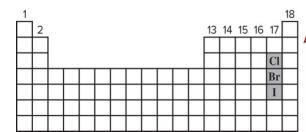
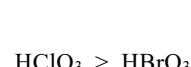
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## Molecular Structure and Oxoacid Strength

- Oxoacids having different central atoms (Z) that are from the same group and that have the same oxidation number. Acid strength increases with increasing electronegativity of Z.



Cl is more electronegative than Br

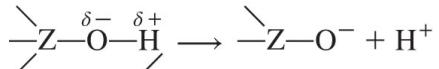


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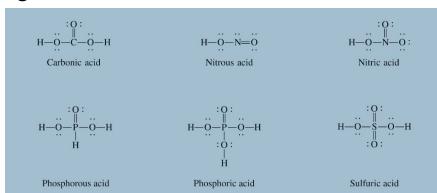
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## Molecular Structure and Oxoacid Strength <sub>2</sub>



The O-H bond will be more polar and easier to break if:

- Z is very electronegative or
- Z is in a high oxidation state



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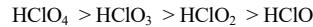
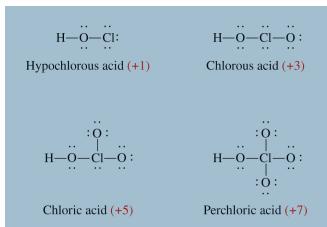
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## Molecular Structure and Oxoacid Strength <sub>3</sub>

2. Oxoacids having the same central atom (Z) but different numbers of attached groups.

Acid strength increases as the oxidation number of Z increases.



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### Example 15.12<sub>1</sub>

Predict the relative strengths of the oxoacids in each of the following groups:

- a) HClO, HBrO, and HIO
- b) HNO<sub>3</sub> and HNO<sub>2</sub>

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### Example 15.12<sub>2</sub>

#### *Strategy*

Examine the molecular structure. In (a) the two acids have similar structure but differ only in the central atom (Cl, Br, and I). Which central atom is the most electronegative? In (b) the acids have the same central atom (N) but differ in the number of O atoms. What is the oxidation number of N in each of these two acids?

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### Example 15.12<sub>3</sub>

*Solution*

- a) These acids all have the same structure, and the halogens all have the same oxidation number (+1). Because the electronegativity decreases from Cl to I, the Cl atom attracts the electron pair it shares with the O atom to the greatest extent. Consequently, the O—H bond is the most polar in HClO and least polar in HIO. Thus, the acid strength decreases as follows:



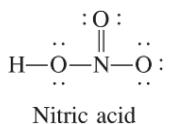
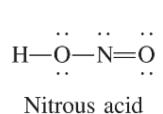
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### Example 15.12<sub>4</sub>

- b) The structures of  $\text{HNO}_3$  and  $\text{HNO}_2$  are shown in Figure 15.5. Because the oxidation number of N is +5 in  $\text{HNO}_3$  and +3 in  $\text{HNO}_2$ ,  $\text{HNO}_3$  is a stronger acid than  $\text{HNO}_2$ .



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## Acid-Base Properties of Salts<sup>1</sup>

**Table 15.7 Acid-Base properties of Salts**

Type of salt	Examples	Ions that undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO <sub>3</sub> , RbBr, BaCl <sub>2</sub>	None	≈7
Cation from strong base; anion from weak acid	CH <sub>3</sub> COONa, KNO <sub>2</sub>	Anion	>7
Cation from weak base; anion from strong acid	NH <sub>4</sub> Cl, NH <sub>4</sub> NO <sub>3</sub>	Cation	<7
Cation from weak base; anion from weak acid	NH <sub>4</sub> NO <sub>2</sub> , CH <sub>3</sub> COONH <sub>4</sub> , NH <sub>4</sub> CN	Anion and cation	<7 if K <sub>b</sub> < K <sub>a</sub> ≈7 if K <sub>b</sub> ≈ K <sub>a</sub> >7 if K <sub>b</sub> > K <sub>a</sub>
Small, highly charged cation; anion from strong acid	AlCl <sub>3</sub> , Fe(NO <sub>3</sub> ) <sub>3</sub>	Hydrated cation	<7

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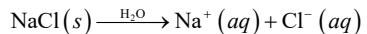
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## Acid-Base Properties of Salts: Neutral and Basic Solutions

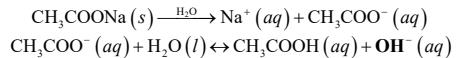
### Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be<sup>2+</sup>) **and** the conjugate base of a **strong** acid (e.g. Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>).



### Basic Solutions:

Salts derived from a strong base **and** a **weak** acid.



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### Example 15.13<sub>1</sub>

Calculate the pH of a 0.15 M solution of sodium acetate ( $\text{CH}_3\text{COONa}$ ). What is the percent hydrolysis?

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### Example 15.13<sub>2</sub>

#### *Strategy*

What is a salt? In solution,  $\text{CH}_3\text{COONa}$  dissociates completely into  $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$  ions. The  $\text{Na}^+$  ion, as we saw earlier, does not react with water and has no effect on the pH of the solution. The  $\text{CH}_3\text{COO}^-$  ion is the conjugate base of the weak acid  $\text{CH}_3\text{COOH}$ . Therefore, we expect that it will react to a certain extent with water to produce  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$ , and the solution will be basic.

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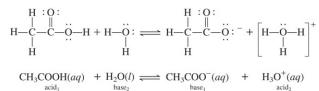
### Example 15.13<sub>3</sub>

**Solution**

*Step 1:* Because we started with a 0.15 M sodium acetate solution, the concentrations of the ions are also equal to 0.15 M after dissociation:

$\text{CH}_3\text{COONa}(\text{aq}) \leftrightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$		
Initial (M):	0.15	0
Change (M):	-0.15	+0.15
Final (M):	0	0.15

Of these ions, only the acetate ion will react with water



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### Example 15.13<sub>4</sub>

At equilibrium, the major species in solution are  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{OH}^-$ .

The concentration of the  $\text{H}^+$  ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

*Step 2:* Let  $x$  be the equilibrium concentration of  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$  ions in mol/L, we summarize:

$\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(l) \leftrightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial (M):	0.15	0.00
Change (M):	- $x$	+ $x$
Equilibrium (M):	0.15- $x$	$x$

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### Example 15.13<sub>5</sub>

*Step 3:* From the preceding discussion and Table 15.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as

$$K_b = \frac{[\text{CH}_3\text{COO}^-][\text{OH}^-]}{[\text{CH}_3\text{COOH}]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Because  $K_b$  is very small and the initial concentration of the base is large, we can apply the approximation  $0.15 - x \approx 0.15$ :

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6}$$

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### Example 15.13<sub>6</sub>

*Step 4:* At equilibrium:

$$[\text{OH}^-] = 9.2 \times 10^{-6} M$$

$$\text{pOH} = -\log(9.2 \times 10^{-6})$$

$$= 5.04$$

$$\text{pH} = 14.00 - 5.04$$

$$= 8.96$$

Thus the solution is basic, as we would expect. The percent hydrolysis is given by

$$\% \text{ hydrolysis} = \frac{9.2 \times 10^{-6} M}{0.15 M} \times 100\%$$

$$= 0.0061\%$$

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### Example 15.13 <sup>7</sup>

**Check**

The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

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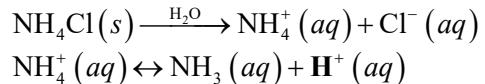
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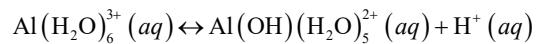
## Acid-Base Properties of Salts: Acidic Solutions

**Acid Solutions:**

Salts derived from a strong acid and a weak base.



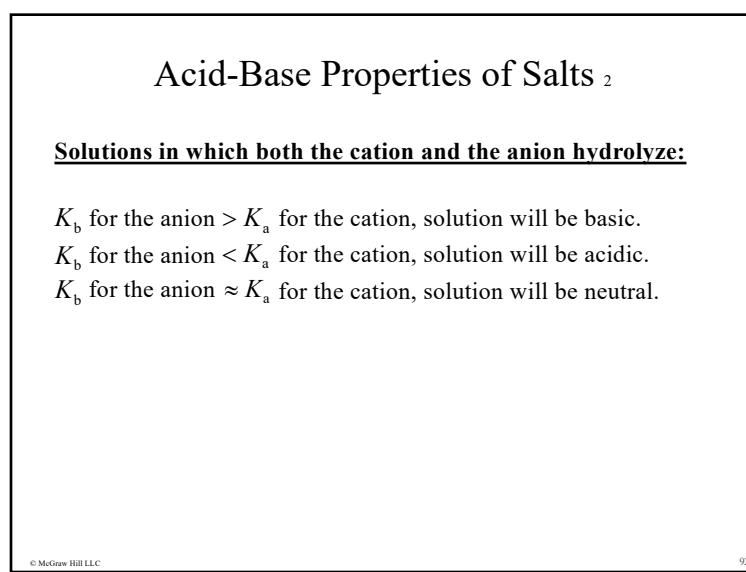
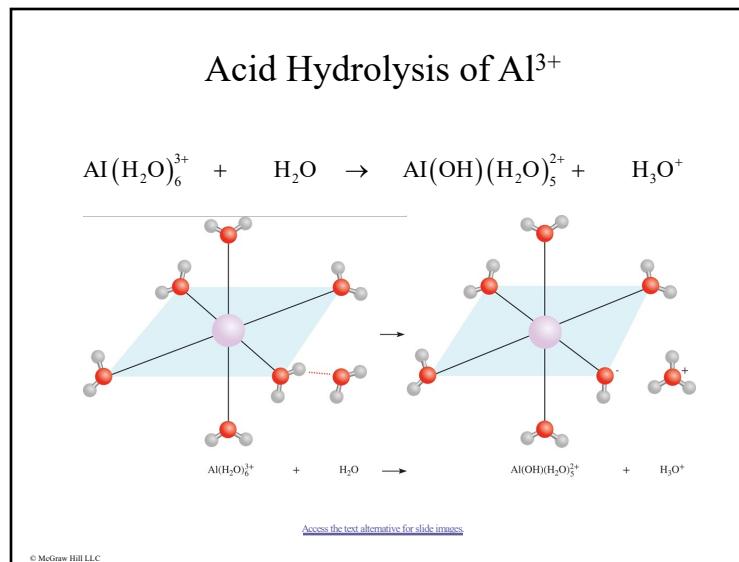
Salts with small, highly charged metal cations (e.g.  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Be}^{2+}$ ) and the conjugate base of a strong acid.



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### Example 15.14<sub>1</sub>

Predict whether the following solutions will be acidic, basic, or nearly neutral:

- (a) NH<sub>4</sub>I
- (b) NaNO<sub>2</sub>
- (c) FeCl<sub>3</sub>
- (d) NH<sub>4</sub>F

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### Example 15.14<sub>2</sub>

#### *Strategy*

In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of  $K_a$  for the cation and  $K_b$  for the anion (see Table 15.7).

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### Example 15.14<sub>3</sub>

*Solution*

We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

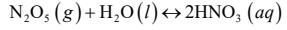
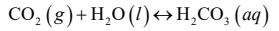
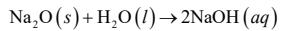
- (a) The cation is  $\text{NH}_4^+$ , which will hydrolyze to produce  $\text{NH}_3$  and  $\text{H}^+$ . The  $\text{I}^-$  anion is the conjugate base of the strong acid  $\text{HI}$ . Therefore,  $\text{I}^-$  will not hydrolyze and the solution is acidic.
- (b) The  $\text{Na}^+$  cation does not hydrolyze. The  $\text{NO}_2^-$  is the conjugate base of the weak acid  $\text{HNO}_2$  and will hydrolyze to give  $\text{HNO}_2$  and  $\text{OH}^-$ . The solution will be basic.

### Example 15.14<sub>4</sub>

- (c)  $\text{Fe}^{3+}$  is a small metal ion with a high charge and hydrolyzes to produce  $\text{H}^+$  ions. The  $\text{Cl}^-$  does not hydrolyze. Consequently, the solution will be acidic.
- (d) Both the  $\text{NH}_4^+$  and  $\text{F}^-$  ions will hydrolyze. From Tables 15.3 and 15.4 we see that the  $K_a$  of  $\text{NH}_4^+$  ( $5.6 \times 10^{-10}$ ) is greater than the  $K_b$  for  $\text{F}^-$  ( $1.4 \times 10^{-11}$ ). Therefore, the solution will be acidic.

## Oxides of the Representative Elements In Their Highest Oxidation States

1	2	Basic oxide			Acidic oxide			Amphoteric oxide								18
Li <sub>2</sub> O	BeO															
Na <sub>2</sub> O	MgO	3	4	5	6	7	8	9	10	11	12	Al <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>	OF <sub>2</sub>	
K <sub>2</sub> O	CaO											Ga <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	SeO <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>
Rb <sub>2</sub> O	SrO											In <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>	Sh <sub>2</sub> O <sub>3</sub>	TeO <sub>3</sub>	I <sub>2</sub> O <sub>3</sub>
Cs <sub>2</sub> O	BaO											Tl <sub>2</sub> O <sub>3</sub>	PbO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	Po <sub>2</sub> O <sub>3</sub>	At <sub>2</sub> O <sub>3</sub>



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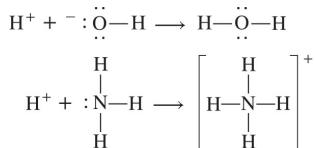
## Definition of An Acid

**Arrhenius acid** is a substance that produces  $\text{H}^+(\text{H}_3\text{O}^+)$  in water.

A **Bronsted acid** is a proton donor.

A **Lewis acid** is a substance that can accept a pair of electrons.

A **Lewis base** is a substance that can donate a pair of electrons.



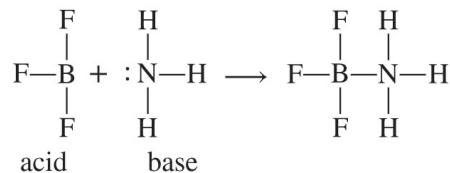
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## Lewis Acids and Bases



No protons donated or accepted!

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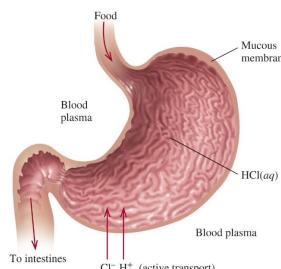
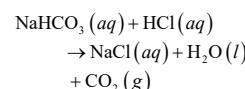
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## Chemistry In Action: Antacids and the Stomach pH Balance

### Some Common Commercial Antacid Preparations

Commercial Name	Active Ingredients
Alka-2	Calcium carbonate
Alka-Seltzer	Aspirin, sodium bicarbonate, citric acid
Bufferin	Aspirin, magnesium carbonate, aluminum glycinate
Buffered aspirin	Aspirin, magnesium carbonate, aluminum hydroxide-glycine
Milk of magnesia	Magnesium hydroxide
Rolaids	Dihydroxy aluminum sodium carbonate
Tums	Calcium carbonate

$$\begin{aligned}
 \text{Mg(OH)}_2(s) + 2\text{HCl}(aq) &\rightarrow \text{MgCl}_2(aq) \\
 &\quad + 2\text{H}_2\text{O}(l)
 \end{aligned}$$


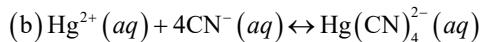
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### Example 15.15<sub>1</sub>

Identify the Lewis acid and Lewis base in each of the following reactions:



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### Example 15.15<sub>2</sub>

#### *Strategy*

In Lewis acid-base reactions, the acid is usually a cation or an electron-deficient molecule, whereas the base is an anion or a molecule containing an atom with lone pairs.

- a) Draw the molecular structure for  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ . What is the hybridization state of Al in  $\text{AlCl}_3$ ?
- b) Which ion is likely to be an electron acceptor? An electron donor?

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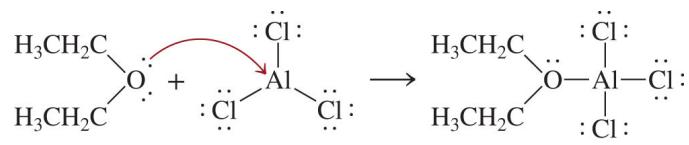
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### Example 15.15<sub>3</sub>

**Solution**

(a) The Al is  $sp^2$ -hybridized in  $\text{AlCl}_3$  with an empty  $2p_z$  orbital. It is electron deficient, sharing only six electrons. Therefore, the Al atom has a tendency to gain two electrons to complete its octet. This property makes  $\text{AlCl}_3$  a Lewis acid. On the other hand, the lone pairs on the oxygen atom in  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  make the compound a Lewis base:



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### Example 15.15<sub>4</sub>

(b) Here the  $\text{Hg}^{2+}$  ion accepts four pairs of electrons from the  $\text{CN}^-$  ions. Therefore,  $\text{Hg}^{2+}$  is the Lewis acid and  $\text{CN}^-$  is the Lewis base.

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