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Acids and Bases

Chapter 15

Chapter Outline

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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.

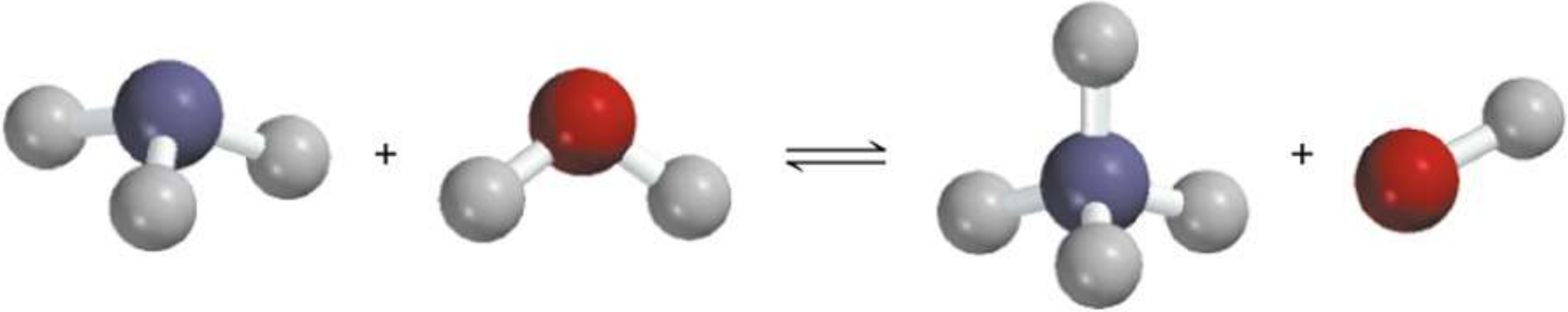
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

A Brønsted **acid** is a proton donor

A Brønsted **base** is a proton acceptor



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

base	acid	$\rightleftharpoons$	acid	base
base	acid		conjugate acid	conjugate base

Example 16.1

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

$$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$$

Example 16.1

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.

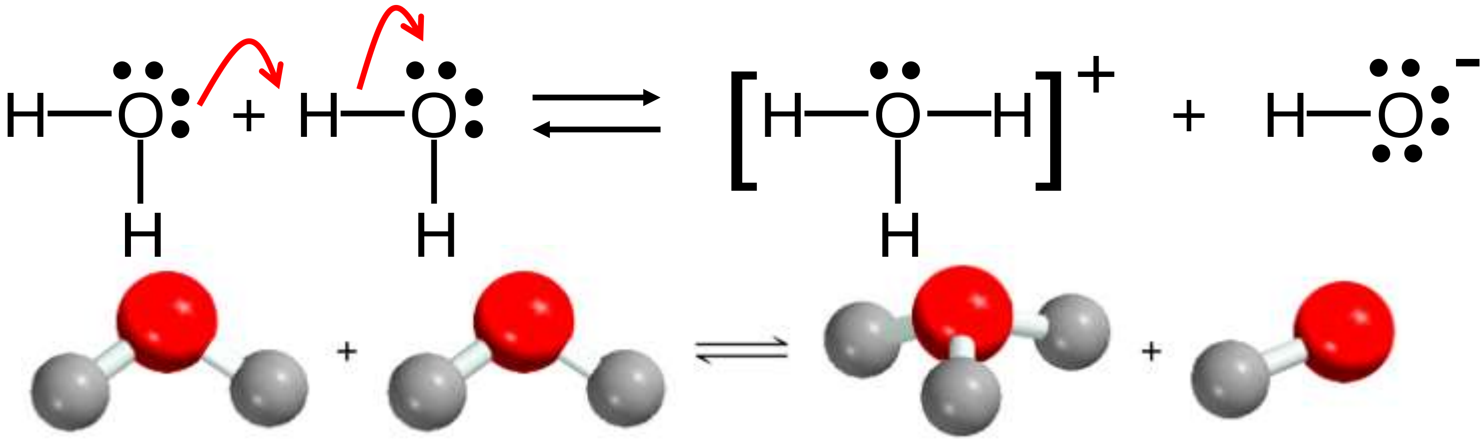
Solution

NH_3 has one fewer H atom and one fewer positive charge than NH_4^+. F^- has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are (1) NH_4^+ and NH_3 and (2) HF and F^-.

Acid-Base Properties of Water

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

autoionization of water



base

conjugate acid

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

acid

conjugate base

The Ion Product of Water

$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$ $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$ $[H_2O] = \text{constant}$

$$K_c[H_2O] = K_w = [H^+][OH^-]$$

The ***ion-product constant*** (***K_w***) is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

At 25^0C
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

	Solution Is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

Example 16.2

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 *M*. Calculate the concentration of H^+ ions.

Example 16.2

Strategy

We are given the concentration of the OH^- ions and asked to calculate $[H^+]$. The relationship between $[H^+]$ and $[OH^-]$ in water or an aqueous solution is given by the ion-product of water, K_w [Equation (16.4)].

Example 16.2

Solution

Rearranging Equation (16.4), we write

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

Check

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

pH – A Measure of Acidity

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

Solution Is		**At 25^0C**	
neutral	$[\mathrm{H}^+] = [\mathrm{OH}^-]$	$[\mathrm{H}^+] = 1.0 \times 10^{-7}$	pH = 7
acidic	$[\mathrm{H}^+] > [\mathrm{OH}^-]$	$[\mathrm{H}^+] > 1.0 \times 10^{-7}$	pH < 7
basic	$[\mathrm{H}^+] < [\mathrm{OH}^-]$	$[\mathrm{H}^+] < 1.0 \times 10^{-7}$	pH > 7

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

Other important relationships

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

$$[\text{H}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$-\log [\text{H}^+] - \log [\text{OH}^-] = 14.00$$

$$\text{pH} + \text{pOH} = 14.00$$

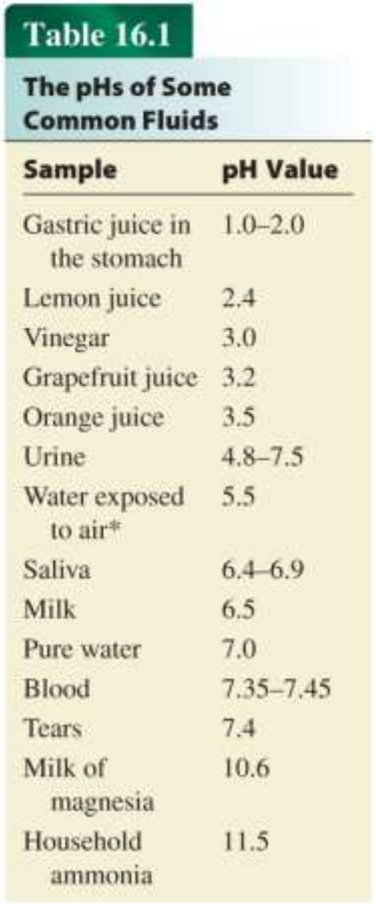


Table 16.1

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

pH Meter

Example 16.3

The concentration of H^+ ions in a bottle of table wine was 3.2×10^{-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 1.0×10^{-3} *M.* Calculate the pH of the wine on these two occasions.

Example 16.3

Strategy

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

Example 16.3

Solution

According to Equation (16.5), pH = -log [H^+]. When the bottle was first opened, [H^+] = 3.2×10^{-4} *M*, which we substitute in Equation (16.5)

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

On the second occasion, [H^+] = 1.0×10^{-3} *M*, so that

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

Example 16.3

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.

Example 16.4

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

Example 16.4

Strategy

Here we are given the pH of a solution and asked to calculate $[H^+]$. Because pH is defined as pH = $-\log [H^+]$, we can solve for $[H^+]$ by taking the antilog of the pH; that is, $[H^+] = 10^{-pH}$, as shown in Equation (16.6).

Example 16.4

Solution

From Equation (16.5)

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

Therefore,

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

To calculate $[\text{H}^+]$, we need to take the antilog of −4.82

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

Example 16.4

Check

Because the pH is between 4 and 5, we can expect [H^+] to be between 1 x 10^{-4} *M* and 1 x 10^{-5} *M*. Therefore, the answer is reasonable.

Example 16.5

In a NaOH solution $[OH^-]$ is 2.9×10^{-4} *M.* Calculate the pH of the solution.

Example 16.5

Strategy

Solving this problem takes two steps. First, we need to calculate pOH using Equation (16.8). Next, we use Equation (16.10) to calculate the pH of the solution.

Solution

We use Equation (16.8):

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

Example 16.5

Now we use Equation (16.10):

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH}$$

$$= 14.00 - 3.54 = \mathbf{10.46}$$

Alternatively, we can use the ion-product constant of water, $K_w = [H^+][OH^-]$ to calculate $[H^+]$, and then we can calculate the pH from the $[H^+]$. Try it.

Check The answer shows that the solution is basic (pH > 7), which is consistent with a NaOH solution.

Strong Electrolyte – 100% dissociation

$$\mathrm{NaCl}\ (s) \xrightarrow{H_2O} \mathrm{Na^+}\ (aq) + \mathrm{Cl^-}\ (aq)$$

Weak Electrolyte – not completely dissociated

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-}\ (aq) + \mathrm{H^+}\ (aq)$$

Strong Acids are strong electrolytes

$$\mathrm{HCl}\ (aq) + \mathrm{H_2O}\ (l) \longrightarrow \mathrm{H_3O^+}\ (aq) + \mathrm{Cl^-}\ (aq)$$

$$\mathrm{HNO_3}\ (aq) + \mathrm{H_2O}\ (l) \longrightarrow \mathrm{H_3O^+}\ (aq) + \mathrm{NO_3^-}\ (aq)$$

$$\mathrm{HClO_4}\ (aq) + \mathrm{H_2O}\ (l) \longrightarrow \mathrm{H_3O^+}\ (aq) + \mathrm{ClO_4^-}\ (aq)$$

$$\mathrm{H_2SO_4}\ (aq) + \mathrm{H_2O}\ (l) \longrightarrow \mathrm{H_3O^+}\ (aq) + \mathrm{HSO_4^-}\ (aq)$$

Weak Acids are weak electrolytes

$$\mathrm{HF}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{F^-}\ (aq)$$

$$\mathrm{HNO_2}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{NO_2^-}\ (aq)$$

$$\mathrm{HSO_4^-}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{SO_4^{2-}}\ (aq)$$

$$\mathrm{H_2O}\ (l) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

Strong Bases are strong electrolytes

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

$$\mathrm{KOH}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{K^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

$$\mathrm{Ba(OH)_2}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ba^{2+}}\ (aq) + \mathrm{2OH^-}\ (aq)$$

Weak Bases are weak electrolytes

$$F^{-}\,(aq) + H_2O\,(l) \rightleftharpoons OH^{-}\,(aq) + HF\,(aq)$$

$$NO_2^{-}\,(aq) + H_2O\,(l) \rightleftharpoons OH^{-}\,(aq) + HNO_2\,(aq)$$

Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqueous solution.

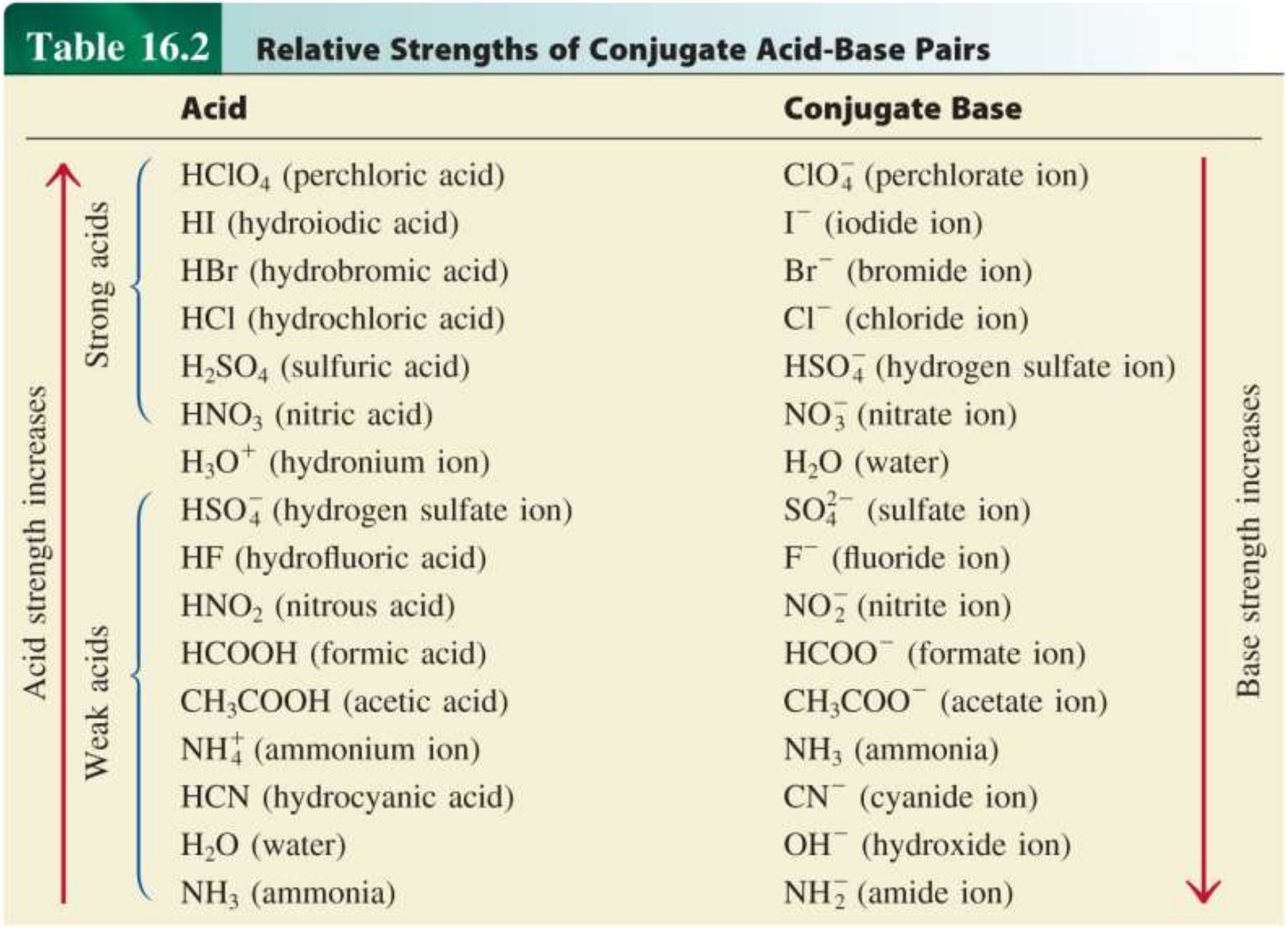


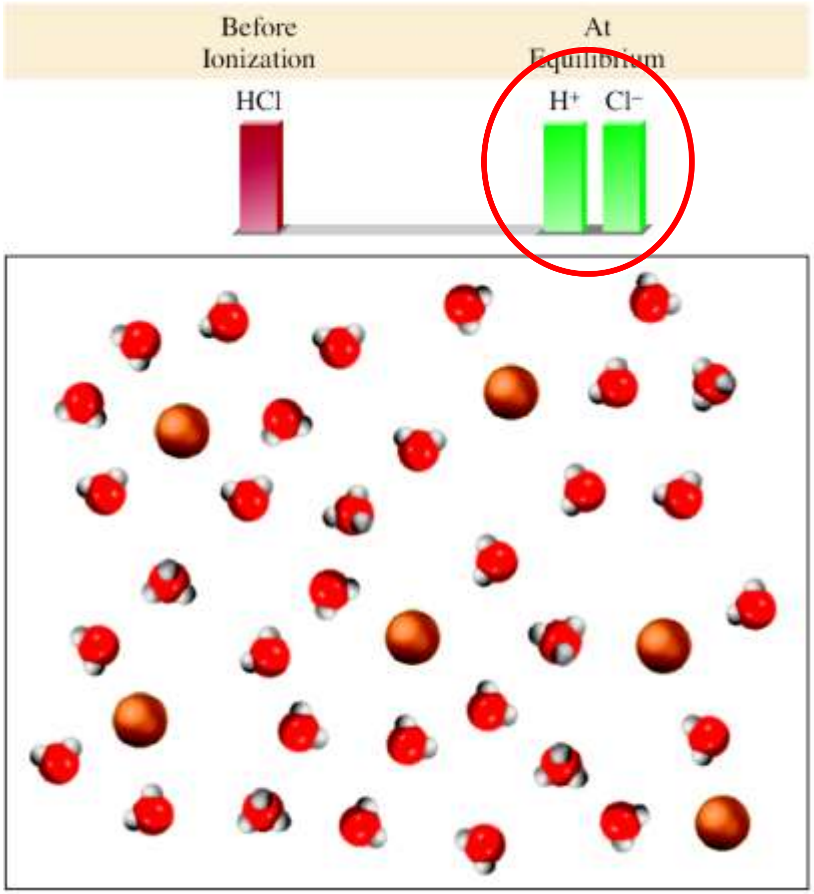
Table 16.2 **Relative Strengths of Conjugate Acid-Base Pairs**

	Acid	**Conjugate Base**
Strong acids	$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)
	HI (hydroiodic acid)	I^- (iodide ion)
	HBr (hydrobromic acid)	Br^- (bromide ion)
	HCl (hydrochloric acid)	Cl^- (chloride ion)
	H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
	HNO_3 (nitric acid)	NO_3^- (nitrate ion)
	H_3O^+ (hydronium ion)	H_2O (water)
Weak acids	HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)
	HF (hydrofluoric acid)	F^- (fluoride ion)
	HNO_2 (nitrous acid)	NO_2^- (nitrite ion)
	HCOOH (formic acid)	$HCOO^-$ (formate ion)
	CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
	NH_4^+ (ammonium ion)	NH_3 (ammonia)
	HCN (hydrocyanic acid)	CN^- (cyanide ion)
	H_2O (water)	OH^- (hydroxide ion)
	NH_3 (ammonia)	NH_2^- (amide ion)

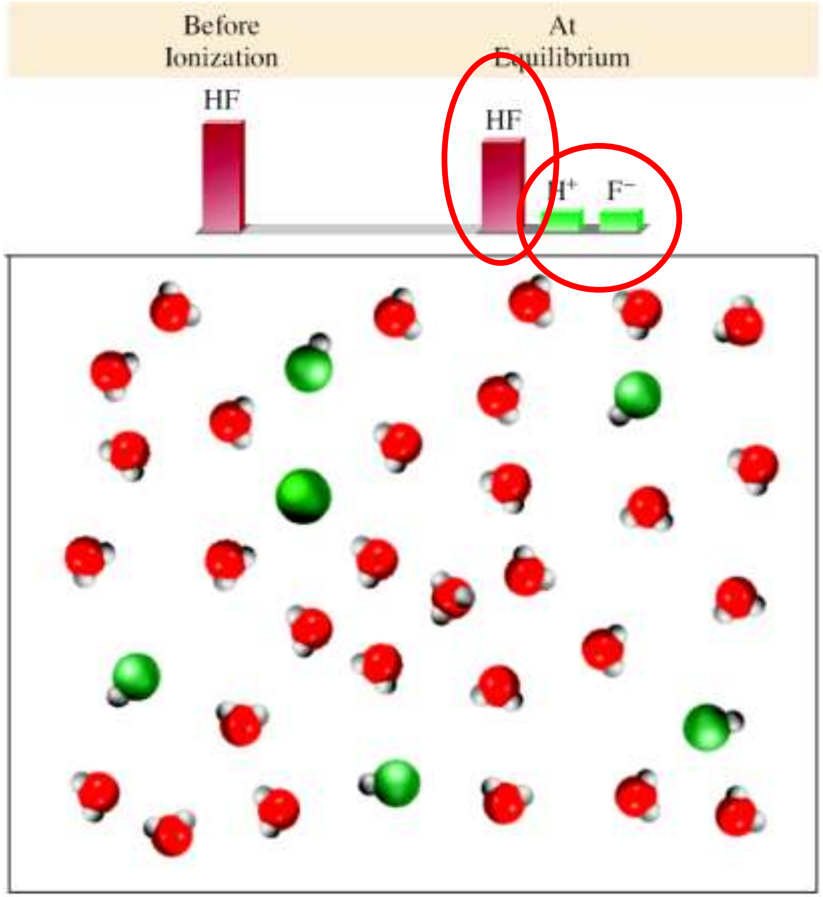
Acid strength increases

Base strength increases

Strong Acid (HCl)



Weak Acid (HF)



Example 16.6

Calculate the pH of a

(a) 1.0×10^{-3} *M* HCl solution

(b) 0.020 *M* $Ba(OH)_2$ solution

Example 16.6

Strategy

Keep in mind that HCl is a strong acid and $Ba(OH)_2$ is a strong base. Thus, these species are completely ionized and no HCl or $Ba(OH)_2$ will be left in solution.

Solution

(a)The ionization of HCl is

$$\mathrm{HCl}(aq) \longrightarrow \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq)$$

Example 16.6

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

	$HCl(aq)$	$\rightarrow$	$H^+(aq)$	+	$Cl^-(aq)$
Initial (*M*):	1.0×10^{-3}		0.0		0.0
Change (*M*):	-1.0×10^{-3}		$+1.0 \times 10^{-3}$		$+1.0 \times 10^{-3}$
Final (*M*):	0.0		1.0×10^{-3}		1.0×10^{-3}

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

$$[H^+] = 1.0 \times 10^{-3}\ M$$

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

$$= \mathbf{3.00}$$

Example 16.6

(b) $Ba(OH)_2$ is a strong base; each $Ba(OH)_2$ unit produces two OH^- ions:

$$Ba(OH)_2(aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

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

	$Ba(OH)_2(aq)$	→	$Ba^{2+}(aq)$	+	$2OH^-(aq)$
Initial (*M*):	0.020		0.00		0.00
Change (*M*):	- 0.020		+ 0.020		+2(0.020)
Final (*M*):	0.00		0.020		0.040

Example 16.6

Thus,

$$[OH^-] = 0.040\ M$$
$$pOH = -\log 0.040 = 1.40$$

Therefore, from Equation (16.10),

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

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

Example 16.7

Predict the direction of the following reaction in aqueous solution:

$$HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2^-(aq)$$

Example 16.7

Strategy

The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO_2^-, or to the left, favoring HNO_2 and CN^-. Which of the two is a stronger acid and hence a stronger proton donor: HNO_2 or HCN? Which of the two is a stronger base and hence a stronger proton acceptor: CN^- or NO_2^-? Remember that the stronger the acid, the weaker its conjugate base.

Example 16.7

Solution

In Table 16.2 we see that HNO_2 is a stronger acid than HCN. Thus, CN^- is a stronger base than NO_2^-. The net reaction will proceed from left to right as written because HNO_2 is a better proton donor than HCN (and CN^- is a better proton acceptor than NO_2^-).

Weak Acids (HA) and Acid Ionization Constants

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

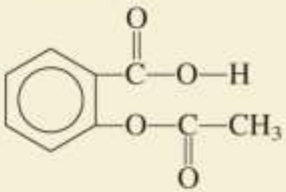
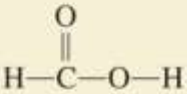
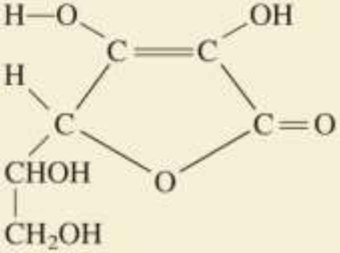
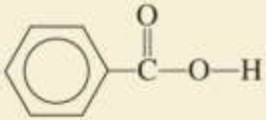
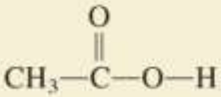
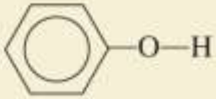
$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$$

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

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

K_a ↑ weak acid strength ↑

Table 16.3 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	$H-F$	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	$O=N-O-H$	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	$HCOOH$	 $H-\overset{\overset{O}{\|}}{C}-O-H$	1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH	 $CH_3-\overset{\overset{O}{\|}}{C}-O-H$	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	$H-C\equiv N$	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

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 $[OH^-]$ because it is determined by $[H^+]$.
2. Use **ICE** (Initial, Change, Equilibrium) 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.

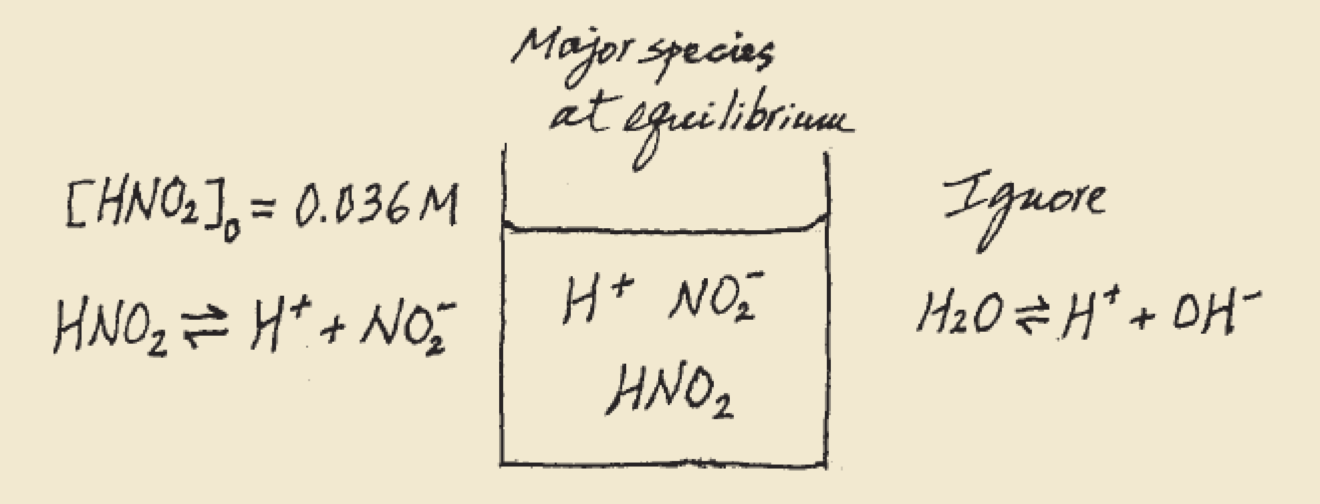
Example 16.8

Calculate the pH of a 0.036 *M* nitrous acid (HNO_2) solution:

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

Example 16.8

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 16.6, we ignore the ionization of H_2O so the major source of H^+ ions is the acid. The concentration of OH^- ions is very small as we would expect from an acidic solution so it is present as a minor species.

Example 16.8

Solution We follow the procedure already outlined.

Step 1: The species that can affect the pH of the solution are HNO_2, H^+, and the conjugate base NO_2^-. We ignore water's contribution to $[H^+]$.

Step 2: Letting *x* be the equilibrium concentration of H^+ and NO_2^- ions in mol/L, we summarize:

	$HNO_2(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$NO_2^-(aq)$
Initial (*M*):	0.036		0.00	0.00
Change (*M*):	$-x$		$+x$	$+x$
Equilibrium (*M*):	$0.036 - x$		x	x

Example 16.8

Step 3: From Table 16.3 we write

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

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

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

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

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

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

Example 16.8

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:

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

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

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

Example 16.8

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

$$[H^+] = 3.8 \times 10^{-3}\ M$$

$$pH = -\log (3.8 \times 10^{-3})$$

$$= \mathbf{2.42}$$

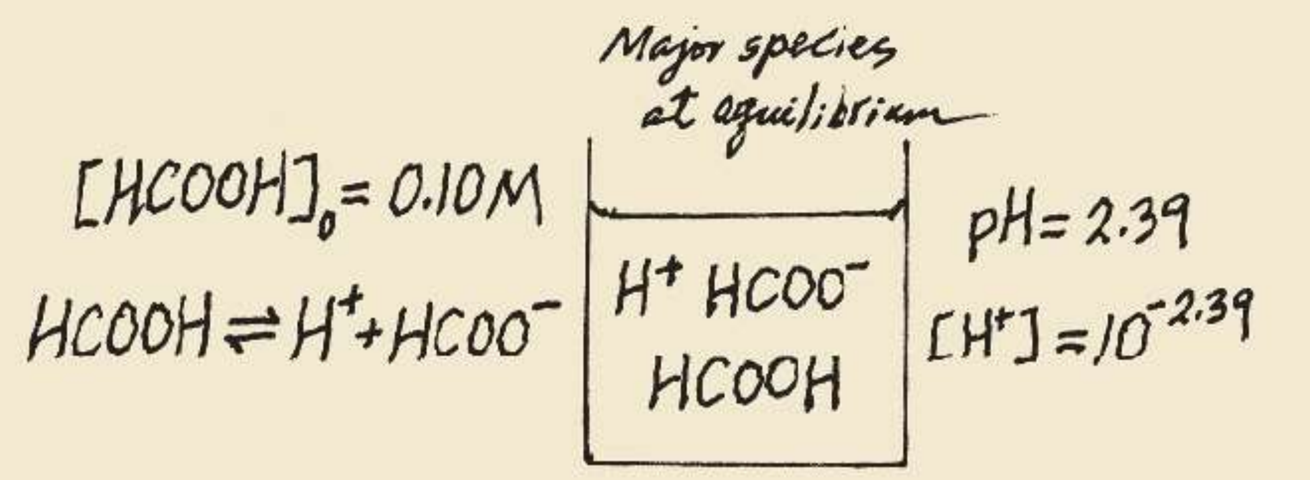
Check Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. Compare the calculated pH with that of a 0.036 *M* strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.

Example 16.9

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

Example 16.9

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.



Example 16.9

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

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

$$2.39 = -\log [H^+]$$

Taking the antilog of both sides, we get

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

Example 16.9

Next we summarize the changes:

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

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

Example 16.9

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

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})}$$

$$= \mathbf{1.8 \times 10^{-4}}$$

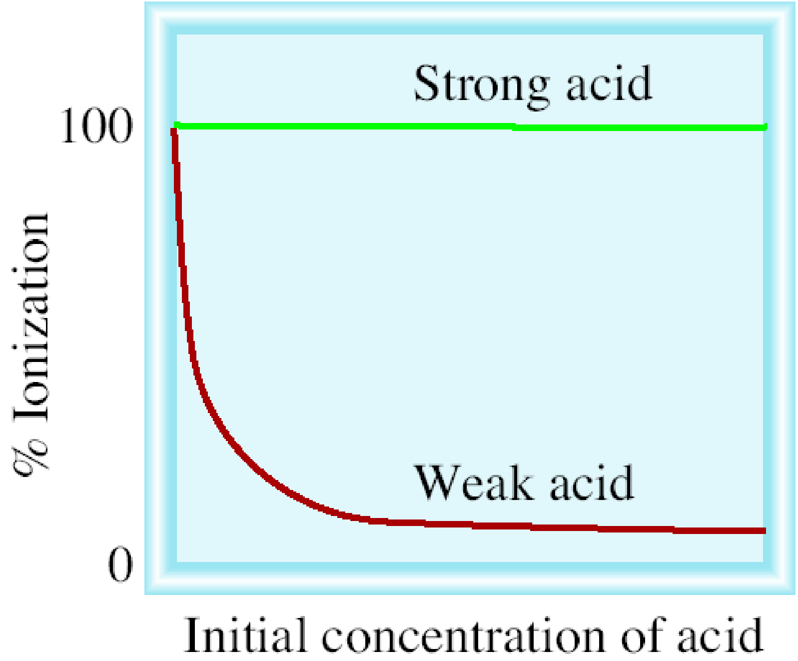
Check

The K_a value differs slightly from the one listed in Table 16.3 because of the rounding-off procedure we used in the calculation.

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

For a monoprotic acid HA,

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



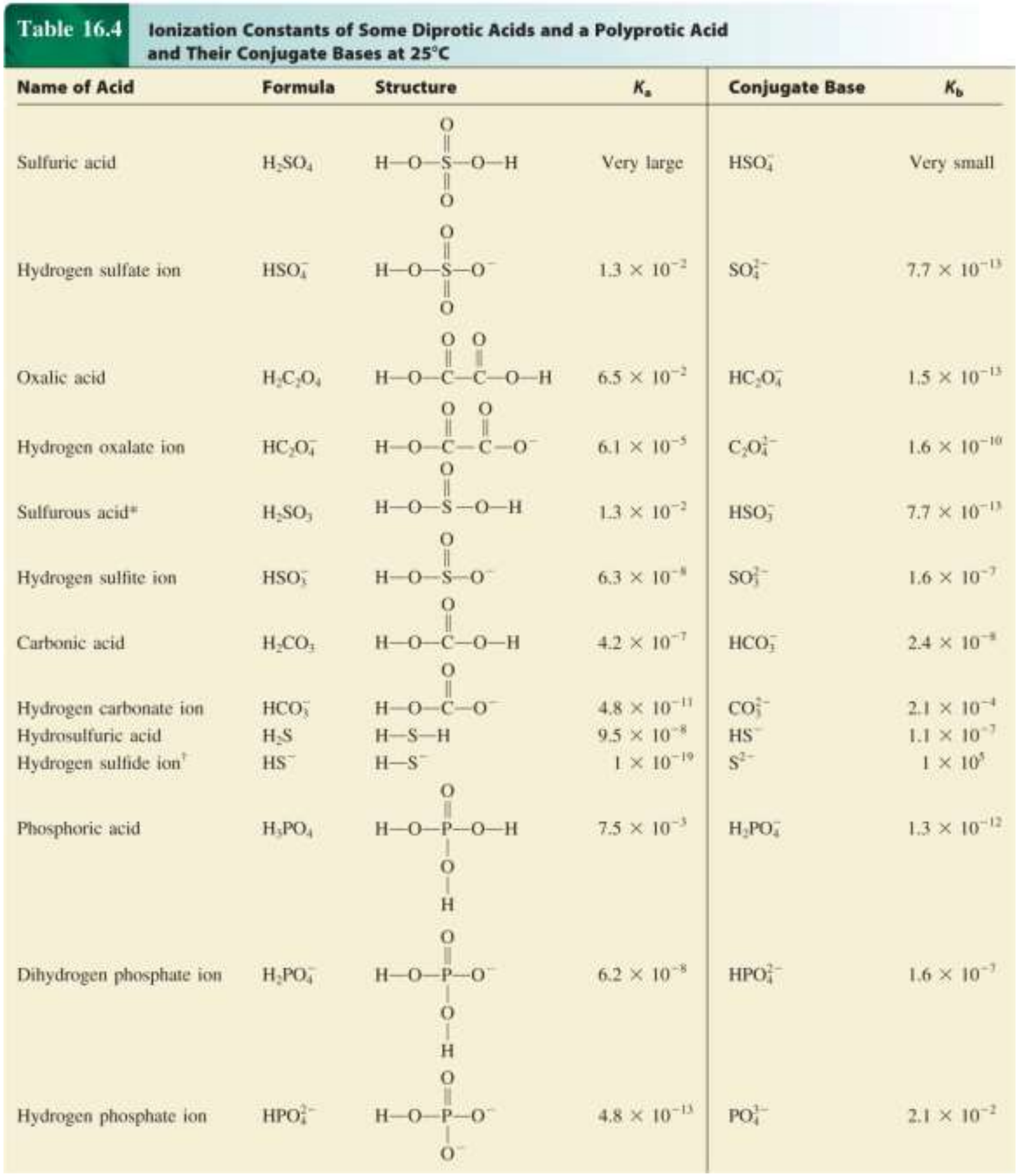


Table 16.4 Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}O{-}H}$	Very large	HSO_4^-	Very small
Hydrogen sulfate ion	HSO_4^-	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}{-}O^{-}}$	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}\overset{\overset{O}{\Vert}}{C}{-}O{-}H}$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}\overset{\overset{O}{\Vert}}{C}{-}O^{-}}$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{S}{-}O{-}H}$	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{S}{-}O^{-}}$	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}O{-}H}$	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{C}{-}O^{-}}$	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	$\mathrm{H{-}S{-}H}$	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion†	HS^-	$\mathrm{H{-}S^{-}}$	1×10^{-19}	S^{2-}	1×10^{5}
Phosphoric acid	H_3PO_4	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{\underset{\underset{H}{\vert}}{O}}{\vert}}{P}}{-}O{-}H}$	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
Dihydrogen phosphate ion	$H_2PO_4^-$	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{\underset{\underset{H}{\vert}}{O}}{\vert}}{P}}{-}O^{-}}$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen phosphate ion	HPO_4^{2-}	$\mathrm{H{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{O^{-}}{\vert}}{P}}{-}O^{-}}$	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}

Weak Bases and Base Ionization Constants

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

K_b ↑ weak base strength ↑

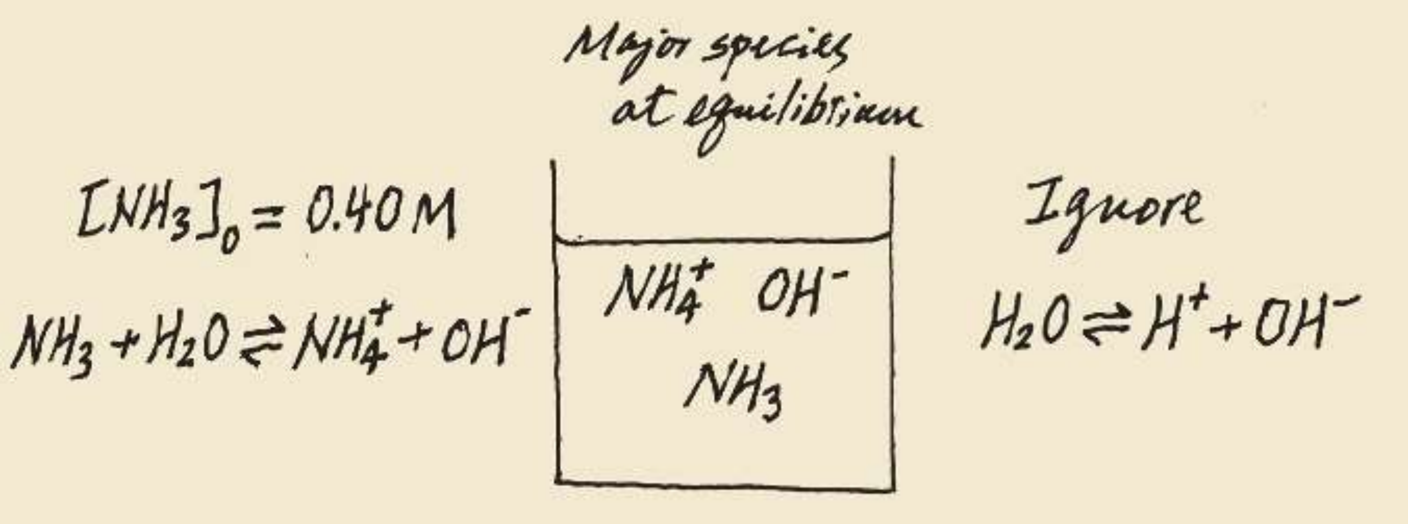
Solve weak base problems like weak acids ***except*** solve for [OH-] instead of [H^+].

Example 16.11

What is the pH of a 0.40 *M* ammonia solution?

Example 16.11

Strategy The procedure here is similar to the one used for a weak acid (see Example 16.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are NH_3, NH_4^+ ,and OH^-. 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:



Example 16.11

Solution We proceed according to the following steps.

Step 1: The major species in an ammonia solution are NH_3, NH_4^+, and OH^-. We ignore the very small contribution to OH^- concentration by water.

Step 2: Letting *x* be the equilibrium concentration of NH_4^+ and OH^- ions in mol/L, we summarize:

	$NH_3(aq)$	$+\ H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	$+$	$OH^-(aq)$
Initial (*M*):	0.40			0.00		0.00
Change (*M*):	$-x$			$+x$		$+x$
Equilibrium (*M*):	$0.40 - x$			x		x

Example 16.11

Step 3: Table 16.5 gives us K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

Applying the approximation $0.40 - x \approx 0.40$, we obtain

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

$$x^2 = 7.2 \times 10^{-6}$$

$$x = 2.7 \times 10^{-3}\ M$$

Example 16.11

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, $[OH^-] = 2.7 \times 10^{-3}$ *M*. Thus,

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

Example 16.11

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.

Ionization Constants of Conjugate Acid-Base Pairs

$$
\begin{array}{lr}
\cancel{HA}\,(aq) \rightleftharpoons H^+\,(aq) + \cancel{A^-}\,(aq) & K_a \\
\cancel{A^-}\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + \cancel{HA}\,(aq) & K_b \\
\hline
H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq) & K_w
\end{array}
$$

$$\boxed{K_aK_b = K_w}$$

Weak Acid and Its Conjugate Base

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

Acid-Base Properties of Salts

Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^-, Br^-, and NO_3^-).

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Basic Solutions:

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

$$CH_3COONa\ (s) \xrightarrow{H_2O} Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + \boxed{OH^-}\ (aq)$$

Example 16.13

Calculate the pH of a 0.25 *M* solution of potassium fluoride (KF). What is the percent hydrolysis?

Example 16.13

Strategy

What is a salt? In solution, KF dissociates completely into K^+ and F^- ions. The K^+ ion does not react with water and has no effect on the pH of the solution because potassium is an alkali metal. The F^- ion is the conjugate base of the weak acid HF (Table 16.3). Therefore, we expect that it will react to a certain extent with water to produce HF and OH^-, and the solution will be basic.

Example 16.13

Solution

Step 1: Because we started with a 0.25 *M* potassium fluoride solution, the concentrations of the ions are also equal to 0.25 *M* after dissociation*:*

	$KF(aq)$	→	$K^+(aq)$ +	$F^-(aq)$
Initial (*M*):	0.25		0	0
Change (*M*):	−0.25		+0.25	+0.25
Final (*M*):	0		0.25	0.25

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

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

Example 16.13

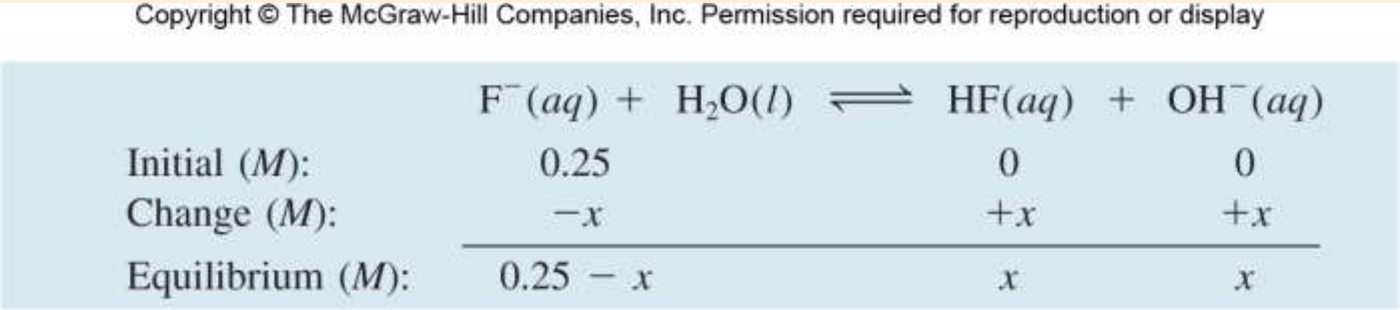
At equilibrium, the major species in solution are HF, F^-, and OH^-. The concentration of the H^+ ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

Step 2: Let x be the equilibrium concentration of HF and OH^- ions in mol/L, we summarize:

	$F^-(aq)$	$+\ H_2O\ (l)$	$\rightleftharpoons$	$HF(aq)$	$+\ OH^-(aq)$
Initial (*M*):	0.25			0.00	0.00
Change (*M*):	$-x$			$+x$	$+x$
Equilibrium (*M*):	$0.25 - x$			x	x

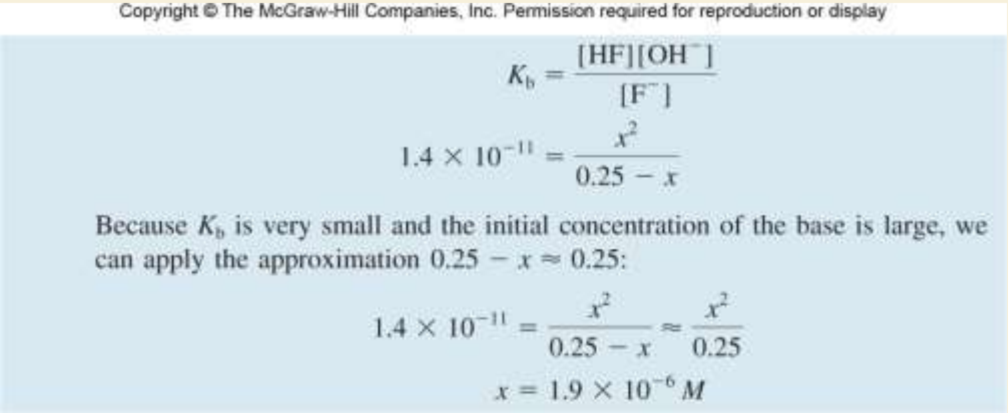
Example 16.13

Step 3: From the preceding discussion and Table 16.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as



	$F^-(aq)$ + $H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	+	$OH^-(aq)$
Initial (M):	0.25		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.25 - x$		x		x

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation 0.25 − *x* ≈ 0.25:



$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$1.4 \times 10^{-11} = \frac{x^2}{0.25 - x}$$

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.25 - x \approx 0.25$:

$$1.4 \times 10^{-11} = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25}$$

$$x = 1.9 \times 10^{-6}\ M$$

Example 16.13

Step 4: At equilibrium:

$$[OH^-] = 1.9 \text{ x } 10^{-6}\ M$$

$$pOH = -\log(1.9 \text{ x } 10^{-6})$$

$$= 5.72$$

$$pH = 14.00 - 5.72$$

$$= 8.28$$

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

$$\% \text{ hydrolysis} = \frac{[F^-]_{\text{hydrolyzed}}}{[F^-]_{\text{initial}}}$$

$$= \frac{1.9 \times 10^{-6}}{0.25} \times 100\%$$

$$= 0.00076\%$$

Example 16.13

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.

Acid-Base Properties of Salts

Acid Solutions:

Salts derived from a strong acid and a weak base.

$$NH_4Cl\ (s) \xrightarrow{H_2O} NH_4^+\ (aq) + Cl^-\ (aq)$$

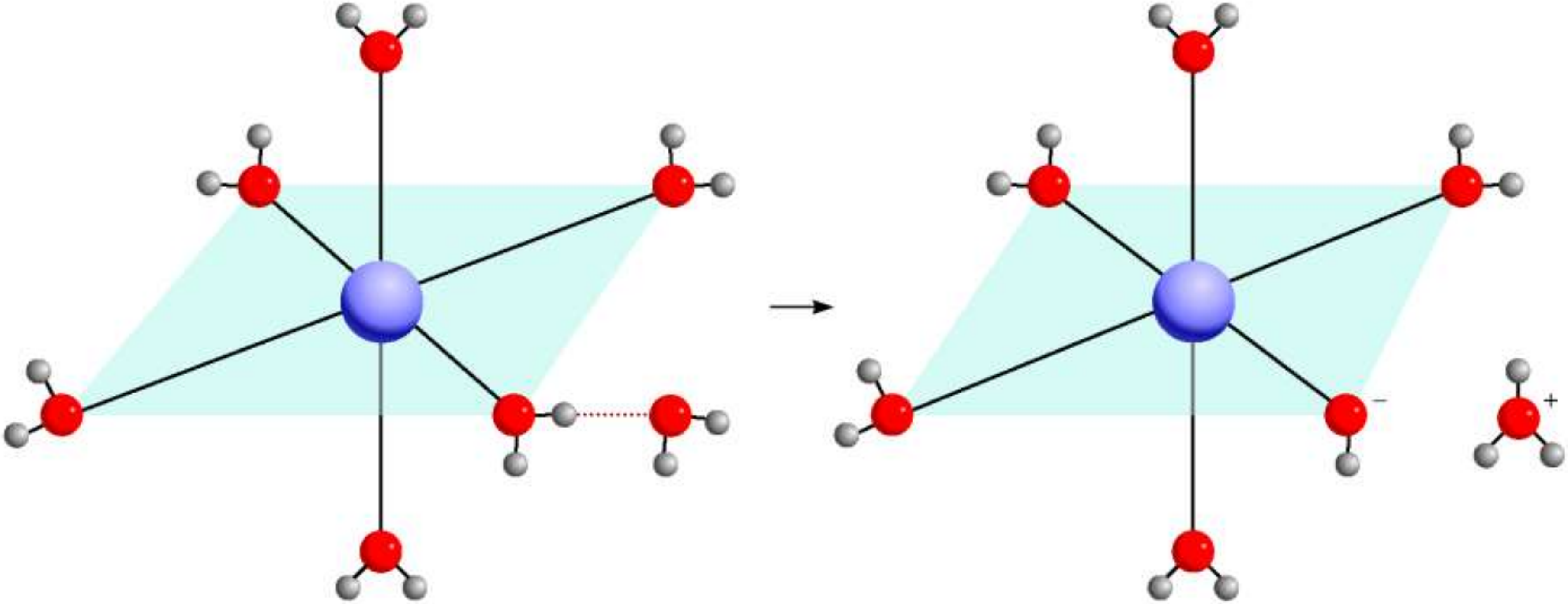
$$NH_4^+\ (aq) \rightleftharpoons NH_3\ (aq) + \boxed{H^+}\ (aq)$$

Salts with small, highly charged metal cations (*e.g.* Al^{3+}, Cr^{3+}, and Be^{2+}) and the conjugate base of a strong acid (for example $AlCl_3$.)

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+\ (aq)$$

Acid Hydrolysis of Al^{3+}

$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(OH)(H_2O)_5^{2+} + H_3O^+$



Acid-Base Properties of Salts

Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion > K_a for the cation, solution will be basic
- K_b for the anion < K_a for the cation, solution will be acidic
- K_b for the anion $\approx$ K_a for the cation, solution will be neutral

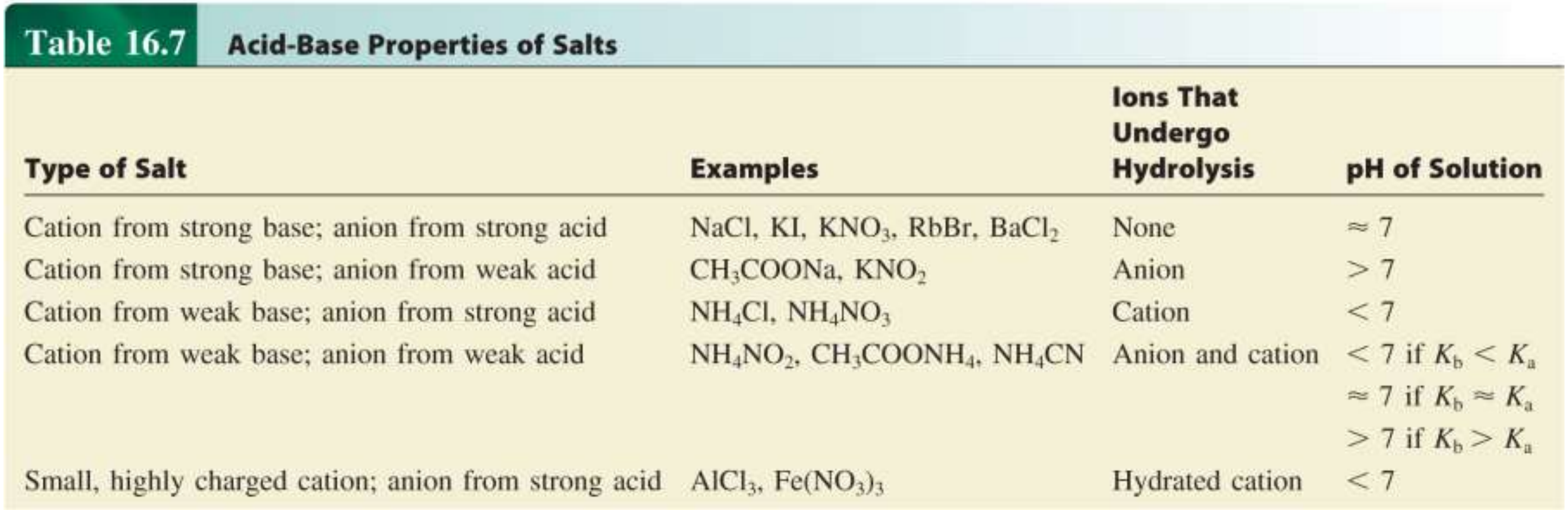


Table 16.7 **Acid-Base Properties of Salts**

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO_3, RbBr, $BaCl_2$	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Fe(NO_3)_3$	Hydrated cation	< 7

Example 16.14

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

(a)NH_4I

(b) $NaNO_2$

(c) $FeCl_3$

(d) NH_4F

Example 16.14

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 16.7).

Example 16.14

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 NH_4^+, which will hydrolyze to produce NH_3 and H^+. The I^- anion is the conjugate base of the strong acid HI. Therefore, I^- will not hydrolyze and the solution is acidic.

(b) The Na^+ cation does not hydrolyze. The NO_2^- is the conjugate base of the weak acid HNO_2 and will hydrolyze to give HNO_2 and OH^-. The solution will be basic.

Example 16.14

(c) Fe^{3+} is a small metal ion with a high charge and hydrolyzes to produce H^+ ions. The Cl^- does not hydrolyze. Consequently, the solution will be acidic.

(d) Both the NH_4^+ and F^- ions will hydrolyze. From Tables 16.5 and 16.3 we see that the K_a of NH_4^+ (5.6×10^{-10}) is greater than the K_b for F^- (1.4×10^{-11}). Therefore, the solution will be acidic.

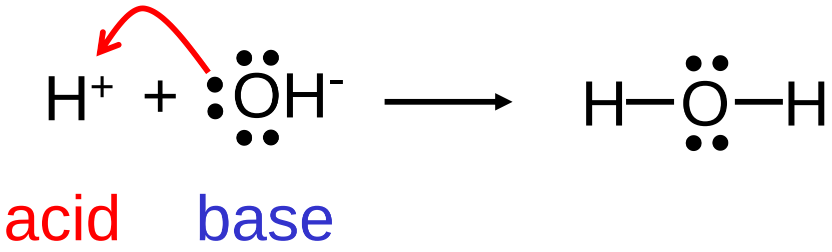
Definition of An Acid

Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

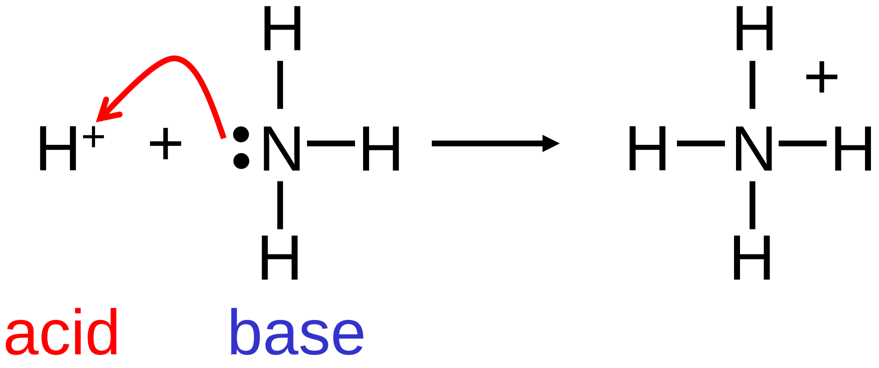
A ***Brønsted acid*** is a proton donor

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

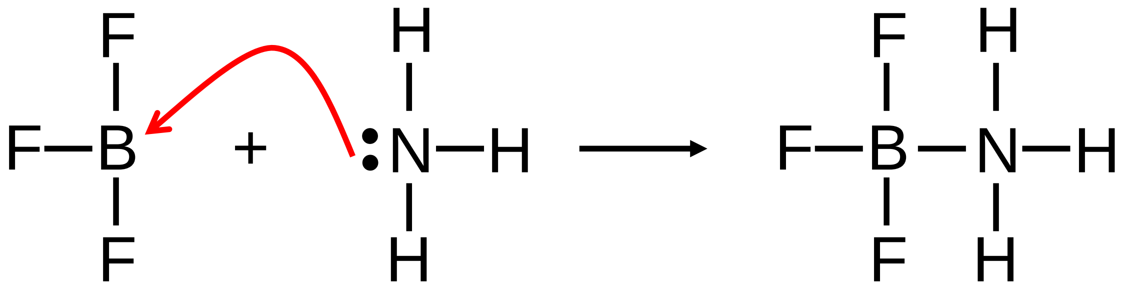


$$H^+ + :\ddot{O}H^- \longrightarrow H{-}\ddot{O}{-}H$$



$$H^+ + :NH_3 \longrightarrow NH_4^+$$

Lewis Acids and Bases



No protons donated or accepted!

Example 16.15

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

(a) $C_2H_5OC_2H_5 + AlCl_3 \rightleftharpoons (C_2H_5)_2OAlCl_3$

(b) $Hg^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Hg(CN)_4^{2-}(aq)$

Example 16.15

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.

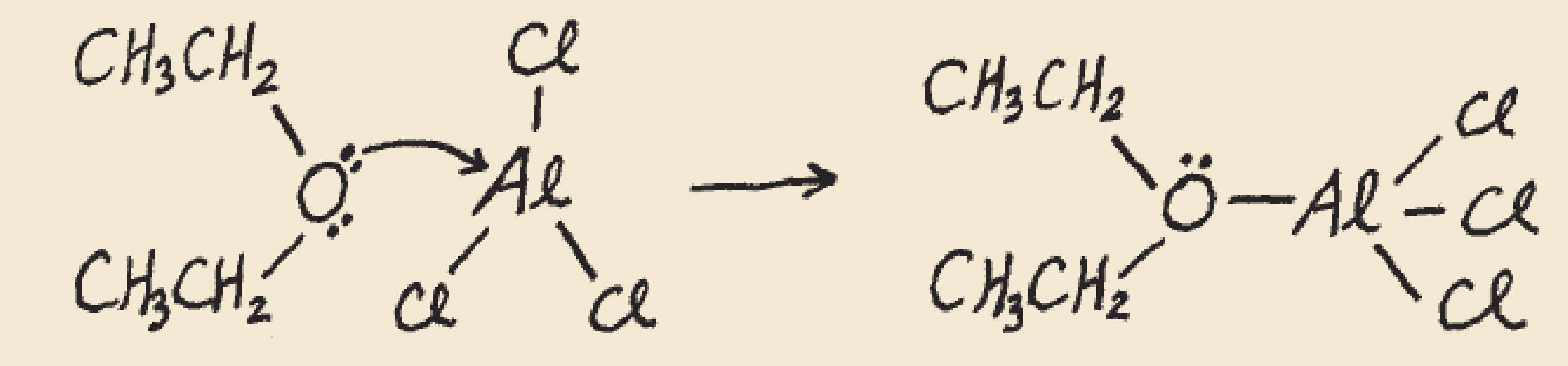
(a) Draw the molecular structure for $C_2H_5OC_2H_5$. What is the hybridization state of Al in $AlCl_3$?

(b) Which ion is likely to be an electron acceptor? An electron donor?

Example 16.15

Solution

(a) The Al is *sp*^{2}-hybridized in $AlCl_3$ 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 $AlCl_3$ a Lewis acid. On the other hand, the lone pairs on the oxygen atom in $C_2H_5OC_2H_5$ make the compound a Lewis base:



Example 16.15

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