

16.7: Finding the $\left[\mathrm{H_{3}0}^{+}\right]$ and pH of Strong and Weak Acid Solutions

Key Concept Video Finding the [H₃O⁺] and pH of Strong and Weak Acid Solutions

In a solution containing a strong or weak acid, there are two potential sources of $\rm H_3O^+$: the ionization of the acid itself and the autoionization of water. If we let HA be a strong or weak acid, the ionization reactions are:

$H_2O(l) + H_2O(l) \rightleftharpoons H_2O^+(aq) + OH^-(aq)$ $K_w = 1.0 \times 10^{-14}$	$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$	Strong or Weak Acid
	$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$	

Except in extremely dilute acid solutions, the autoionization of water contributes a negligibly small amount of H_3O^+ compared to the ionization of the strong or weak acid. Recall from Section 16.6. that autoionization in pure water produces an H_3O^+ concentration of $1.0 \times 10^{-7}M$. In a strong or weak acid solution, the additional H_3O^+ from the acid causes the autoionization of water equilibrium to shift left (as described by Le Châtelier's principle). Consequently, in most strong or weak acid solutions, the autoionization of water produces even less H_3O^+ than in pure water and can be ignored. Therefore, we can focus exclusively on the amount of H_3O^+ produced by the acid.

Strong Acids

Because strong acids, by definition, completely ionize in solution, and because we can (in nearly all cases) ignore the contribution of the autoionization of water, the concentration of H_3O^+ in a strong acid solution is equal to the concentration of the strong acid. For example, a 0.10 M HCl solution has an H_3O^+ concentration of 0.10 M and a pH of 1.00:

$$0.10~\textrm{M HCl} \Rightarrow \left[\textrm{H}_{\textrm{3}}\textrm{O}^{+}\right] = 0.10~\textrm{M} \Rightarrow \textrm{pH} = -\log(0.10) = 1.00$$

The only exceptions are extremely dilute (10^{-5}M) strong acid solutions.

Weak Acids

Determining the pH of a weak acid solution is more complicated because the concentration of $\rm H_3O^+$ is *not equal* to the concentration of the weak acid. For example, if we make solutions of 0.10 M HCl (a strong acid) and 0.10 M acetic acid (a weak acid) in the laboratory and measure the pH of each, we get the following results:

$$0.10 \text{ M HCl}$$
 pH = 1.00
 $0.10 \text{ M HC}_2\text{H}_3\text{O}_2$ pH = 2.87

The pH of the acetic acid solution is higher (it is less acidic) because acetic acid only partially ionizes.

Calculating the $\left[H_3O^+\right]$ formed by the ionization of a weak acid requires solving an equilibrium problem similar to those in Chapter 15. Consider, for example, a 0.10-M solution of the generic weak acid HA with an acid ionization constant K_a . Since we can ignore the contribution of the autoionization of water, we only have to determine the concentration of H₃O⁺ formed by the following equilibrium:

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

We can summarize the initial conditions, the changes, and the equilibrium conditions in the following ICE table:

	[HA]	[H ₃ O ⁺]	[A-]
Initial	0.10	≈0.00	0.00
Change	-x	+ <i>x</i>	+ x
Equilibrium	0.10 - x	х	х

ICE tables were first introduced in Section 15.6 \square . The reactant $H_2O(l)$ is a pure liquid and is therefore not included in either the equilibrium constant expression or the ICE table (see Section 15.5[□]).

In the table, we list the initial H₂O⁺ concentration as approximately zero because of the negligibly small contribution of $\mathrm{H_3O^+}$ due to the autoionization of water (discussed previously). The variable x represents the amount of HA that ionizes.

As discussed in Chapter 15^L, each equilibrium concentration is the sum of the two entries above it in the ICE table. In order to find the equilibrium concentration of H₃O, we must find the value of the variable x. We can use the equilibrium expression to set up an equation in which x is the only variable:

$$K_a = \frac{\left[1,0^+\right]\left[A^-\right]}{\left[HA\right]}$$

$$= \frac{x^2}{0.10-x}$$

As is often the case with equilibrium problems, we arrive at a quadratic equation in x, which we can solve using the quadratic formula. However, in many cases we can apply the x is small approximation (first discussed in Section 15.8 □).

In Examples 16.5 and 16.6 we examine the general procedure for solving weak acid equilibrium problems. In both of these examples, the *x* is *small* approximation works well. In Example 16.7 , we solve a problem in which the x is small approximation does not work. In such cases, we can solve the quadratic equation explicitly, or we can apply the method of successive approximations (also discussed in Section 15.8 . Finally, in Example 16.8 . we work a problem in which we find the equilibrium constant of a weak acid from its pH.

Example 16.5 Finding the $\left[H_3O^+\right]$ of a Weak Acid Solution

PROCEDURE FOR Finding the pH (or $[H_3O^+]$ of a Weak Acid Solution

To solve these types of problems, follow the procedure outlined below.

Find the $\left[H_{3}O^{+}\right]$ of a 0.100 M HCN solution.

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

$$HCN(aq) + H_2O(l) \rightleftharpoons$$

 $H_3O^+(aq) + CN^-(aq)$

	[HCN]	[H ₃ O ⁺]	[CN ⁻]
Initial	0.100	≈0.00	0.00
Change			
Equil			

2. Represent the change in the concentration of H₃O + with the variable x. Define the changes in the concentrations of the other reactants and products in terms of x. Always keep in mind the stoichiometry of the reaction.

$$HCN(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + CN^-(aq)$$

	[HCN]	[H ₃ O ⁺]	[CN-]
Initial	0.100	≈ 0.00	0.00
Change	-x	+x	+ <i>x</i>
Equil		0	

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x.

$$HCN(aq) + H_2O(l) \Longrightarrow$$

 $H_3O^+(aq) + CN^-(aq)$

	[HCN]	[H ₃ O ⁺]	[CN-]
Initial	0.100	≈0.00	0.00
Change	-x	+x	+ <i>x</i>
Equil	0.100 - x	Х	х

4. Substitute the expressions for the equilibrium concentrations (from Step 3) into the expression for the acid ionization constant (K_a) .

In many cases, you can make the approximation that x is small (as discussed in Section 15.8 \square). Substitute the value of the acid ionization constant (from Table 16.5 \square) into the K_a expression and solve for x.

Confirm that the *x* is *small* approximation is valid by calculating the ratio of *x* to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{CN}^{-1}\right]}{[\text{HCN}]}$$

$$= \frac{x^2}{0.100 - x} (x \text{ is small})$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.100}$$

$$\sqrt{4.9 \times 10^{-10}} = \sqrt{\frac{x^2}{0.100}}$$

$$x = \sqrt{(0.100)(4.9 \times 10^{-10})}$$

$$= 7.0 \times 10^{-6}$$

$$\frac{7.0 \times 10^{-6}}{0.100} \times 100 \% = 7.0 \times 10^{-3} \%$$

Therefore, the approximation is valid.

5. Determine the $\left[\mathrm{H_3O^+}\right]$ from the calculated value of x and calculate the pH if necessary.

$$\left[H_3 O^+ \right] = 7.0 \times 10^{-6} M$$

(pH was not asked for in this problem.)

6. Check your answer by substituting the calculated equilibrium values into the acid ionization **expression.** The calculated value of K_a should match the given value of K_a . Note that rounding errors and the x is small approximation could result in a difference in the least significant digit when comparing values of K_a .

$$K_a = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{CN}^-\right]}{\left[\text{HCN}\right]} = \frac{\left(7.0 \times 10^{-6}\right)^2}{0.100}$$

= 4.9×10^{-10}

Since the calculated value of K_a matches the given value, the answer is valid.

FOR PRACTICE 16.5 Find the H₃O⁺ concentration of a 0.250 M hydrofluoric acid solution.

Example 16.6 Finding the pH of a Weak Acid Solution

Find the pH of a 0.200 M HNO₂ solution.

PROCEDURE FOR Finding the pH (or H_3O^+) of a Weak Acid Solution

To solve these types of problems, follow the procedure outlined below.

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration. Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

$$HNO_2(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + NO_2^-(aq)$$

	[HNO ₂]	[H ₃ O ⁺]	[NO ₂ ⁻]
Initial	0.200	≈0.00	0.00
C hange			

2. Represent the change in the concentration of H₃O⁺ with the variable x. Define the changes in the concentrations of the other reactants and products in terms of x. Always keep in mind the stoichiometry of the reaction.

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

	[HNO ₂]	[H ₃ O ⁺]	[NO ₂ ⁻]
Initial	0.200	≈0.00	0.00
Change	-x	+x	+x
Equil			

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable *x*.

$$HNO_2(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + NO_2^-(aq)$$

	[HNO ₂]	[H ₃ O ⁺]	[NO ₂ ⁻]
Initial	0.200	≈ 0.00	0.00
C hange	-x	+x	+x
Equil	0.200 x	X	X

4. Substitute the expressions for the equilibrium concentrations (from Step 3) into the expression for the acid ionization constant (K_a) .

In many cases, you can make the approximation that x is small (as discussed in Section 15.8 \square). Substitute the value of the acid ionization constant (from Table 16.5 \square) into the K_a expression and

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a = \frac{\left[\text{H}_3\text{O}^+\right] \left[\text{NO}_2^-\right]}{\left[\text{HNO}_2\right]}$$

$$= \frac{x^2}{0.200 - x} (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{0.200}$$

$$\sqrt{4.6 \times 10^{-4}} = \sqrt{\frac{x^2}{0.200}}$$

$$x = \sqrt{\left(0.200\right) \left(4.6 \times 10^{-4}\right)}$$

$$= 9.6 \times 10^{-3}$$

$$\frac{9.6 \times 10^{-3}}{0.200} \times 100 \% = 4.8 \%$$

Therefore, the approximation is valid (but barely so).

solve for x.

$$\begin{bmatrix} H_3O^+ \end{bmatrix} = 9.6 \times 10^{-3}M$$

$$pH = -\log[H_3O^+]$$

$$= -\log(9.6 \times 10^{-3})$$

$$= 2.02$$

6. Check your answer by substituting the calculated equilibrium values into the acid ionization expression. The calculated value of K_a should match the given value of K_a . Note that rounding errors and the x is small approximation could result in a difference in the least significant digit when comparing values of K_a .

$$K_a = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{NO}_2^-\right]}{\left[\text{HNO}_2\right]} = \frac{\left(9.6 \times 10^{-3}\right)^2}{0.200}$$

= 4.6×10^{-4}

Since the calculated value of K_a matches the given value, the answer is valid.

FOR PRACTICE 16.6

Find the pH of a 0.0150 M acetic acid solution.

Interactive Worked Example 16.5 Finding the [H₃O+] of a Weak Acid Solution

Example 16.7 Finding the pH of a Weak Acid Solution in Cases Where the *x is small* Approximation Does Not Work

Find the pH of a 0.100 M HClO₂ solution.

SOLUTION

1. Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing the given concentration of the weak acid as its initial concentration.
(Note that the H₃O⁺ concentration is listed as approximately zero. Although a little H₃O⁺ is present from the autoionization of water, this amount is negligibly small compared to the amount of H₃O⁺ produced by the acid.)

$$HClO_2(aq) + H_2O(1) \Longrightarrow H_3O^+(aq) + ClO_2^-(aq)$$

	[HClO ₂]	[H ₃ O ⁺]	[ClO ₂ ⁻]
Initial	0.100	≈0.00	0.00
Change			
Equil			

2. Represent the change in $\left[\mathrm{H_3O}^+\right]$ with the variable x. Define the changes in the concentrations of the other reactants and products in terms of x.

	[HClO ₂]	[H ₃ O ⁺]	[ClO ₂ ⁻]
Initial	0.100	≈0.00	0.00
Change	-x	+ <i>x</i>	+ <i>x</i>
Equil			

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x.

$$HClO_2(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + ClO_2^-(aq)$$

	[HClO ₂]	[H ₃ O ⁺]	[ClO ₂ ⁻]
Initial	0.100	≈0.00	0.00
Change	-x	+ <i>x</i>	+ <i>x</i>
Eguil	0.100 - x	Х	X

4. Substitute the expressions for the equilibrium concentrations (from Step 3) into the expression for the acid ionization constant (K_a) . Make the x is small approximation and substitute the value of the acid ionization constant (from Table 16.5 \square) into the K_a expression. Solve for xCheck to see if the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_{a} = \frac{\left[\text{H}_{3}\text{O}^{+}\right]\left[\text{CIO}_{2}^{-}\right]}{\left[\text{HCIO}_{2}\right]}$$

$$= \frac{x^{2}}{0.100 - x} (x \text{ is small})$$

$$0.011 = \frac{x^{2}}{0.100}$$

$$\sqrt{0.011} = \sqrt{\frac{x^{2}}{0.100}}$$

$$x = \sqrt{(0.100)(0.011)} = 0.033$$

$$\frac{0.033}{0.100} \times 100\% = 33\% \text{ Therefore, the } x \text{ is } \text{small}$$

approximation is not valid.

If the x is small approximation is not valid, solve the quadratic equation explicitly or use the method of successive approximations to find x. In this case, we solve the quadratic equation.

$$0.011 = \frac{x^2}{0.100 - x}$$

$$0.011(0.100 - x) = x^2$$

$$0.0011 - 0.011x = x^2$$

$$x^2 + 0.011x - 0.0011 = 0$$

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

$$= \frac{-(0.011) \pm \sqrt{(0.011)^2 - 4(1)(-0.0011)}}{2(11)}$$

$$= \frac{-0.11 \pm 0.067 - 2}{2}$$

$$x = -0.039 \text{ or } x = 0.028$$

Since x represents the concentration of H_3O^+ and since concentrations cannot be negative, we reject the negative root.

x = 0.028

5. Determine the H_3O^+ concentration from the calculated value of x and calculate the pH.

$$H_3O^+$$
 = 0.028M
 $pH = -log [H_3O^+]$
= $-log 0.039$
= 1.55

6. Check your answer by substituting the calculated equilibrium values into the acid ionization expression. The calculated value of K_a should match the given value of K_a . Note that rounding errors could result in a difference in the least significant digit when comparing values of K_a .

$$K_a = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{CIO}_2^-\right]}{\left[\text{HCIO}_2\right]} = \frac{0.028^2}{0.100 - 0.028} = 0.011$$

Since the calculated value of K_a matches the given value, the answer is valid.

FOR PRACTICE 16.7 Find the pH of a 0.010 M HNO₂ solution.

Interactive Worked Example 16.7 Finding the pH of a Weak Acid Solution in Cases Where the x is small Approximation Does Not Work

Example 16.8 Finding the Equilibrium Constant from pH

A 0.100 M weak acid (HA) solution has a pH of 4.25. Find K_a for the acid.

SOLUTION

Use the given pH to find the equilibrium concentration of H₃O⁺. Then write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table showing all known concentrations.

$$\begin{array}{lll} \text{pH} & = & -\log \left[\text{H}_3 \text{O}^+ \right] \\ \\ 4.25 & = & -\log \left[\text{H}_3 \text{O}^+ \right] \\ \\ \left[\text{H}_3 \text{O}^+ \right] & = & 5.6 \times 10^{-5} \text{M} \\ \\ \text{HA}(aq) & + & \text{H}_2 \text{O}(I) = \text{H}_3 \text{O}^+ (aq) + \text{A}^- (aq) \end{array}$$

	[HA]	[H ₃ O ⁺]	[A-]
Initial	0.100	≈0.00	0.00
C hange			
Equil		5.6×10^{-5}	

Use the equilibrium concentration of H₂O⁺ and the stoichiometry of the reaction to predict the changes and equilibrium concentration for all species. For most weak acids, the initial and equilibrium concentrations of the weak acid (HA) are equal because the amount that ionizes is usually very small compared to the initial concentration.

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

	[HA]	[H ₃ O ⁺]	$[A^-]$
Initial	0.100	≈ 0.00	0.00
C hange	-5.6×10^{-5}	+5.6 × 10 ⁻⁵	$+5.6 \times 10^{-5}$
Equil	$(0.100 - 5.6 \times 10^{-5}) \approx 0.100$	5.6×10^{-5}	5.6 × 10 ⁻⁵

Substitute the equilibrium concentrations into the expression for K_a and calculate its value.

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[A^{-}\right]}{[HA]}$$

$$= \frac{\left(5.6 \times 10^{-5}\right)\left(5.6 \times 10^{-5}\right)}{0.100}$$

$$= 3.1 \times 10^{-8}$$

FOR PRACTICE 16.8 A 0.175 M weak acid solution has a pH of 3.25. Find K_a for the acid.

Interactive Worked Example 16.8 Finding the Equilibrium Constant from pH

Conceptual Connection 16.6 The x is small Approximation

Conceptual Connection 16.7 Strong and Weak Acids

Percent Ionization of a Weak Acid

We can quantify the ionization of a weak acid according to the percentage of acid molecules that actually ionize. We define the **percent ionization** $^{\mathfrak{D}}$ of a weak acid as the ratio of the ionized acid concentration to the initial acid concentration, multiplied by 100%:

$$percent ionization = \frac{concentration \ of \ ionized \ acid}{initial \ concentration \ of \ acid} \times 100\% = \frac{\left[H_3O^+\right]_{equil}}{\left[HA\right]_{init}} \times 100\%$$

Because the concentration of ionized acid is equal to the ${\rm H_3O}^+$ concentration at equilibrium (for a monoprotic acid), we can use ${\rm [H_3O}^+]$ equil and ${\rm [HA]}_{\rm init}$ in the formula to calculate the percent ionization. For instance, in Example 16.6^{LD}, we found that a 0.200 M HNO₂ solution contains $9.6\times10^{-3}{\rm M\,H_3O}^+$. The 0.200 M HNO₂ solution therefore has the following percent ionization:

$$\% \ ionization \ = \frac{\left[\,H_3O^{\,+} \,\right]_{equil}}{\left[\,HA \,\right]_{init}} \times 100 \,\% \ = \frac{9.6 \times 10^{\,-3} \,M}{0.200 \,M} \times 100 \,\% \ = 4.8 \,\%$$

As we can see, the percent ionization is relatively small. In this case, even though HNO_2 has the second largest K_a in Table 16.5., less than five molecules out of one hundred ionize. For most other weak acids (with smaller K_a values) the percent ionization is even less.

In Example 16.9 \square , we calculate the percent ionization of a more concentrated HNO₂ solution. In the example, notice that the calculated H₃O⁺ concentration is much greater (as we would expect for a more concentrated solution), but the *percent ionization* is actually smaller.

Example 16.9 Finding the Percent Ionization of a Weak Acid

Find the percent ionization of a $2.5~\mathrm{M}$ HNO $_2$ solution.

SOLUTION

To find the percent ionization, you must find the equilibrium concentration of H_3O^+ . Follow the procedure in Example 16.5, shown in condensed form here.

$$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$$

	[HNO ₂]	[H ₃ O ⁺]	[NO ₂ ⁻]
Initial	2.5	≈0.00	0.00
Change	-x	+ <i>x</i>	+ <i>x</i>
Equil	2.5 - x	х	X

$$K_a = \frac{\left[H_3O^+\right] \left[NO_2^-\right]}{\left[HNO_2\right]} = \frac{x^2}{2.5 - x} (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{2.5}$$

$$x = 0.024$$

Therefore,
$$\left[H_3 O^+ \right] = 0.034 \text{ M}.$$

Use the definition of percent ionization to calculate it. (Since the percent ionization is less than 5%, the *x* is *small* approximation is valid.)

% ionization =
$$\frac{\left[H_30^+\right]_{equil}}{\left[HA\right]_{inff}} \times 100\%$$
=
$$\frac{0.034M}{2.5M} \times 100\% = 1.4\%$$

FOR PRACTICE 16.9 Find the percent ionization of a 0.250 M HC₂H₃O₂ solution.

Interactive Worked Example 16.9 Finding the Percent Ionization of a Weak Acid

We can summarize the results of Examples 16.6 and 16.9 ::

[HNO ₂]	[H ₃ O ⁺]	Percent Ionization
0.200	0.0096	4.8%
2.5	0.034	1.4%

The trend you can see in the above table applies to all weak acids.

- The equilibrium H₃O⁺ concentration of a weak acid increases with increasing initial concentration of the
 acid.
- The percent ionization of a weak acid decreases with increasing concentration of the acid.

In other words, as the concentration of a weak acid solution increases, the concentration of the hydronium ion also increases, but the increase is not linear. The $\rm H_3O^+$ concentration increases more slowly than the concentration of the acid because as the acid concentration increases, a smaller fraction of weak acid molecules ionizes.

ionization equilibrium:

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

1mol dissolved particles 2 mol dissolved particles

If we dilute a weak acid solution initially at equilibrium, the system (according to Le Châtelier's principle) responds to minimize the disturbance. The equilibrium shifts to the right because the right side of the equation contains more particles in solution (2 mol versus 1 mol) than the left side. If the system shifts to the right, the percent ionization is greater in the more dilute solution, which is what we observe.

Conceptual Connection 16.8 Percent Ionization

Mixtures of Acids

Determining the pH of a mixture of acids may seem difficult at first. However, in many cases, the relative strengths of the acids in the mixture allow us to neglect the weaker acid and focus only on the stronger one. Here, we consider two possible acid mixtures: a strong acid with a weak acid and a weak acid with another weak acid.

A Strong Acid and a Weak Acid

Consider a mixture that is 0.10 M in HCl and 0.10 M in HCHO $_2$. There are three sources of $\rm H_3O^+$ ions: the strong acid (HCl), the weak acid (HCHO₂) and the autoionization of water.

$$\begin{split} & \text{HCI}(aq) + \text{H}_2\text{O}(l) \to \text{H}_3\text{O}^+(aq) + \text{CI}^-(aq) & \text{Strong} \\ & \text{HCHO}_2 + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CHO}_2^-(aq) & K_g = 1.8 \times 10^{-4} \\ & \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) & K_w = 1.0 \times 10^{-14} \end{split}$$

Since HCl is strong, we know that it completely ionizes to produce a significant concentration of ${\rm H_3O}^+(0.10~{\rm M})$. The ${
m H_3O}^+$ formed by HCl then *suppresses* the formation of additional ${
m H_3O}^+$ formed by the ionization of HCHO2 or the autoionization of water. In other words, a cording to Le Châtelier's principle, the formation of H_3O^+ by the strong acid causes the weak acid to ionize even less than it would in the absence of the strong acid. To see this clearly, we can calculate $[H_3O^+]$ and $[CHO_2^-]$ in this solution.

In an initial estimate of $[H_3O^+]$, we can neglect the contribution of $HCHO_2$ and H_2O . The concentration of H_3O^+ is then equal to the initial concentration of HCl:

$$\left[\mathrm{H_{3}O}^{+}\right] = \left[\mathrm{HCl}\right] = 0.10 \; \mathrm{M}$$

To find $[CHO_2^{-J}]$, we must solve an equilibrium problem. However, the initial concentration of H_3O^+ in this case is not negligible (as it has been in all the other weak acid equilibrium problems that we have worked so far) because HCl has formed a significant amount of $\rm H_3O^+$. The concentration of $\rm H_3O^+$ formed by HCl becomes the initial concentration of H₃O⁺ in the ICE table for HCHO₂, as shown here:

$$\text{HCHO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CHO}_2^-(aq)$$

	[НСНО2]	[H ₃ O ⁺]	[CHO ₂ ⁻]
Initial	0.10	0.10	0.00
Change	-x	+x	+ <i>x</i>
Fauil	0.10 - x	0.10 + x	x

$$K_a = \frac{\left[H_3O^+\right]\left[CHO_2^-\right]}{\left[HCHO_2\right]}$$

$$= \frac{(0.10+x)x}{0.10-x}$$

Since the equilibrium constant is small relative to the initial concentration of the acid, we can make the x is small approximation:

$$K_a = \frac{(0.10 + x)x}{0.10 - x}$$

$$1.8 \times 10^{-4} = \frac{(0.10)x}{0.10}$$

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

We check the *x* is small approximation and find it is valid:

$$\frac{1.8 \times 10^{-4}}{0.10} \times 100 \% = 0.18 \%$$

Therefore, $\left[\text{CHO}_{2}^{-} \right] = 1.8 \times 10^{-4} \text{M}$. We can now see that we can completely ignore the ionization of the weak acid $(HCHO_2)$ in calculating $[H_3O^+]$ for the mixture. The contribution to the concentration of H_3O^+ by the weak acid must necessarily be equal to the concentration of CHO₂⁻ that we just calculated (because of the stoichiometry of the ionization reaction). Therefore, we have the following contributions to $|H_3O^+|$:

HCl contributes 0.10 M.

 $HCHO_2$ contributes 1.8×10^{-4} M or 0.00018 M.

Total
$$\left[H_3O^+\right]$$
 = 0.10 M + 0.00018 M = 0.10 M.

As we can see, because the significant figure rules for addition limit the answer to two decimal places, the amount of ${\rm H_3O}^+$ contributed by ${\rm HCHO_2}$ is completely negligible. The amount of ${\rm H_3O}^+$ contributed by the autoionization of water is even smaller and therefore similarly negligible.

A Mixture of Two Weak Acids

When we mix two weak acids, we again have three potential sources of ${\rm H_3O^+}$ to consider: each of the two weak acids and the autoionization of water. However, if the K_a values of the two weak acids are sufficiently different in magnitude (if they differ by more than a factor of several hundred), then as long as the concentrations of the two acids are similar in magnitude (or the concentration of the stronger one is greater than that of the weaker), we can assume that the weaker acid will not make a significant contribution to the concentration of H₃O⁺. We make this assumption for the same reason that we made a similar assumption for a mixture of a strong acid and a weak one: The stronger acid suppresses the ionization of the weaker one, in accordance with Le Châtelier's principle. Example 16.10

shows how to calculate the concentration of H₃O⁺ in a mixture of two weak acids.

Example 16.10 Mixtures of Weak Acids

Find the pH of a mixture that is 0.300 M in HF and 0.100 M in HClO.

SOLUTION

The three possible sources of H₃O⁺ ions are HF, HClO, and H₂O. Write the ionization equations for the three sources and their corresponding equilibrium constants. Because the equilibrium constant for the ionization of HF is about 24,000 times larger than that for the ionization of HClO, the contribution of HF to $[H_3O^+]$ is by far the greatest. You can therefore calculate the $[H_3O^+]$ formed by HF only and neglect the other two potential sources of H₃O +.

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$
 $K_a = 6.8 \times 10^{-4}$

$$\begin{split} & \text{HCl}(aq) + \text{H}_2\text{O}(l) = & \text{H}_3\text{O}^+(aq) + \text{ClO}^-(aq) \\ & \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) = & \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \\ \end{split} \qquad & K_a = 2.9 \times 10^{-8} \\ & \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) = & \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \\ \end{split}$$

Write the balanced equation for the ionization of HF and use it as a guide to prepare an ICE table.

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

	[HF]	[H ₃ O ⁺]	[F ⁻]
Initial	0.300	≈0.00	0.00
Change	-x	+ <i>x</i>	+x
Equil	0.300 - x	х	х

Substitute the expressions for the equilibrium concentrations into the expression for the acid ionization constant (K_a) . Because the equilibrium constant is small relative to the initial concentration of HF, you can make the *x* is small approximation. Substitute the value of the acid ionization constant (from Table 16.5) into the K_a expression and solve for x.

Confirm that the *x* is *small* approximation is valid by calculating the ratio of *x* to the number it was subtracted from in the approximation. The ratio must be less than 0.05 (or 5%).

$$K_a = \frac{\left[H_3O^+\right]\left[F^-\right]}{\left[HF\right]} = \frac{x^2}{0.300 - x} (x \text{ is small})$$

$$6.8 \times 10^{-4} = \frac{x^2}{0.300}$$

$$\sqrt{(0.300)\left(6.8 \times 10^{-4}\right)} = \sqrt{x^2}$$

$$x = 1.4 \times 10^{-3}$$

$$\frac{1.4 \times 10^{-3}}{0.300} \times 100 \% = 4.7 \%$$

Therefore, the approximation is valid (though barely so).

Determine the H_3O^+ concentration from the calculated value of x and find the pH.

$$[H_3O^+] = 1.4 \times 10^{-3}M$$

 $pH = -\log(1.4 \times 10^{-3}) = 1.85$

Find the ClO- concentration of the above mixture of HF and HClO.

Conceptual Connection 16.9 Judging Relative pH

Aot for Distribution

Aot for Distribution

Aot for Distribution

Processing math: 43%