35. At 25°C, the relationship: \([\text{H}^+] \cdot [\text{OH}^-] = K_w = 1.0 \times 10^{-14}\) always holds for aqueous solutions. When \([\text{H}^+]\) is greater than \(1.0 \times 10^{-7} \text{M}\), then the solution is acidic; when \([\text{H}^+]\) is less than \(1.0 \times 10^{-7} \text{M}\), then the solution is basic; when \([\text{H}^+] = 1.0 \times 10^{-7} \text{M}\), then the solution is neutral. In terms of [OH\(^-\)], an acidic solution has [OH\(^-\)] < \(1.0 \times 10^{-7} \text{M}\), a basic solution has [OH\(^-\)] > \(1.0 \times 10^{-7} \text{M}\) and a neutral solution has [OH\(^-\)] = \(1.0 \times 10^{-7} \text{M}\).

a. \([\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} \text{M}; \) The solution is neutral.

b. \([\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12} \text{M}; \) The solution is acidic.

c. \([\text{OH}^-] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-10}} = 4.0 \times 10^{-5} \text{M}; \) The solution is basic.

d. \([\text{OH}^-] = \frac{1.0 \times 10^{-14}}{6.1} = 1.6 \times 10^{-15} \text{M}; \) The solution is acidic.

41. a. \([\text{H}^+] = 10^{-pH}, \ [\text{H}^+] = 10^{-pH} = 10^{-7.41} = 3.9 \times 10^{-8} \text{M}\)

\(\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.41 = 6.59; \) \([\text{OH}^-] = 10^{-\text{pOH}} = 10^{-6.59} = 2.6 \times 10^{-7} \text{M}\)

or \([\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{3.9 \times 10^{-8}} = 2.6 \times 10^{-7} \text{M}\)

b. \([\text{H}^+] = 10^{-15.3} = 5 \times 10^{-16} \text{M}; \) \(\text{pOH} = 14.00 - 15.3 = -1.3; \) \([\text{OH}^-] = 10^{-\text{pOH}} = 10^{-(-1.3)} = 20 \text{M}\)

c. \([\text{H}^+] = 10^{-(-1.0)} = 10 \text{M}; \) \(\text{pOH} = 14.00 - (-1.0) = 15.0; \) \([\text{OH}^-] = 10^{-15.0} = 1 \times 10^{-15} \text{M}\)

d. \([\text{H}^+] = 10^{-3.2} = 6 \times 10^{-4} \text{M}; \) \(\text{pOH} = 14.00 - 3.2 = 10.8; \) \([\text{OH}^-] = 10^{-10.8} = 2 \times 10^{-11} \text{M}\)

e. \([\text{OH}^-] = 10^{-5.0} = 1 \times 10^{-5} \text{M}; \) \(\text{pH} = 14.0 - \text{pOH} = 14.0 - 5.0 = 9.0; \) \([\text{H}^+] = 10^{-9.0} = 1 \times 10^{-9} \text{M}\)

f. \([\text{OH}^-] = 10^{-9.6} = 3 \times 10^{-10} \text{M}; \) \(\text{pH} = 14.0 - 9.6 = 4.4; \) \([\text{H}^+] = 10^{-4.4} = 4 \times 10^{-5} \text{M}\)

46. HClO\(_4\) and HNO\(_3\) are strong acids to memorize. As in Exercise 14.45, 0.250 \text{M} solutions of these strong acids give 0.250 \text{M} H\(^+\) and 0.250 \text{M} A\(^-\) where A\(^-\) is the conjugate base of the strong acid.

a. Major species = H\(^+\), ClO\(_4\)\(^-\) and H\(_2\)O; \(\text{pH} = -\log[H^+] = -\log(0.250) = 0.602\)

b. Major species = H\(^+\), NO\(_3\)\(^-\) and H\(_2\)O; \(\text{pH} = 0.602\)

47. Strong acids are assumed to completely dissociate in water: HCl(aq) → H\(^+\)(aq) + Cl\(^-\)(aq)

a. A 0.10 \text{M} HCl solution gives 0.10 \text{M} H\(^+\) and 0.10 \text{M} Cl\(^-\) since HCl completely dissociates. The amount of H\(^+\) from H\(_2\)O will be insignificant.

\(\text{pH} = -\log[H^+] = -\log(0.10) = 1.00\)

b. 5.0 \text{M} H\(^+\) is produced when 5.0 \text{M} HCl completely dissociates. The amount of H\(^+\) from H\(_2\)O will be insignificant. \(\text{pH} = -\log(5.0) = -0.70\) (Negative pH values just indicate very concentrated acid solutions).

c. \(1.0 \times 10^{-11} \text{M} H^+\) is produced when 1.0 \times 10^{-11} \text{M} HCl completely dissociates. If you take the negative log of \(1.0 \times 10^{-11}\) this gives pH = 11.00. This is impossible! We dissolved an acid in water and got a basic pH. What we must consider in this problem is that water by itself donates \(1.0 \times 10^{-7} \text{M} H^+\). We can normally ignore the small amount of H\(^+\) from H\(_2\)O except when we have a very dilute solution of an acid (as in the case here). Therefore, the pH is that of neutral water (pH = 7.00) since the amount of HCl present is insignificant.
Major species: HC$_2$H$_3$O$_2$ ($K_a = 1.8 \times 10^{-5}$) and water; Major source of $H^+ = HC_2H_3O_2$. Since $K_a$ for HC$_2$H$_3$O$_2$ is less than one, then HC$_2$H$_3$O$_2$ is a weak acid and we must solve an equilibrium problem to determine $[H^+]$. The set-up is:

$$\begin{align*}
HC_2H_3O_2 & \rightleftharpoons H^+ + C_3H_3O_2^- \\
\text{Initial} & \quad 0.20 \, M \quad \sim 0 \quad 0 \\
\text{Change} & \quad -x \quad \rightarrow \quad +x \quad +x \\
\text{Equil.} & \quad 0.20 - x \quad x \quad x
\end{align*}\n$$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+] [C_3H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20} \quad (\text{assuming } x \ll 0.20)$$

$$x = [H^+] = 1.9 \times 10^{-3} \, M$$

We have made two assumptions which we must check.

1. $0.20 - x \approx 0.20$

$$(x/0.20) \times 100 = (1.9 \times 10^{-3}/0.20) \times 100 = 0.95\%$. Good assumption (1% error). If the percent error in the assumption is $< 5\%$, then the assumption is valid.

2. Acetic acid is the major source of $H^+$, i.e., we can ignore $10^{-7} \, M \, H^+$ already present in neutral $H_2O$.

$[H^+]$ from $HC_2H_3O_2 = 1.9 \times 10^{-3} >> 10^{-7}$; This assumption is valid.

In future problems we will always begin the problem solving process by making these assumptions and we will always check them. However, we may not explicitly state that the assumptions are valid. We will always state when the assumptions are not valid and we have to use other techniques to solve the problem. Remember, anytime we make an assumption, we must check its validity before the solution to the problem is complete. Answering the question:

$$[H^+] = [C_2H_3O_2^-] = 1.9 \times 10^{-3} \, M; \quad [OH^-] = 5.3 \times 10^{-12} \, M$$

$$[HC_2H_3O_2] = 0.20 - x = 0.198 \approx 0.20 \, M; \quad \text{pH} = -\log (1.9 \times 10^{-3}) = 2.72$$
Chapter 14: Acids and Bases

57. Boric acid is a weak acid; it is the major source of $\text{H}^+$. 

$$\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_4^- + \text{H}^+$$

Initial $0.50\, M$ $0$ $\sim 0$

Change $-x$ $ightarrow$ $+x$ $+x$

Equil. $0.50 - x$ $x$ $x$

$$K_a = 5.8 \times 10^{-10} = \frac{[\text{B(OH)}_4^-][\text{H}^+]}{[\text{B(OH)}_3]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} \quad \text{(assuming } x \ll 0.50)$$

$$x = [\text{H}^+] = 1.7 \times 10^{-5} \, M; \quad \text{pH} = 4.77 \quad \text{Assumptions good (} x \text{ is } 3.4 \times 10^{-3}\% \text{ of } 0.50).$$

58. This is a weak acid in water. We must solve the weak acid problem.

$$12.2 \, g \, \text{C}_6\text{H}_5\text{CO}_2\text{H (HBz)} \times \frac{1 \, \text{mol} \, \text{HBz}}{122.12 \, g} = 9.99 \times 10^{-2} \, \text{mol} ; \quad [\text{HBz}]_0 = 9.99 \times 10^{-2} \, M$$

$$\text{HBz} \rightleftharpoons \text{H}^+ + \text{Bz}^- \quad \text{Bz}^- = \text{C}_6\text{H}_5\text{CO}_2^-$$

Initial $9.99 \times 10^{-2} \, M$ $\sim 0$ $0$

Change $-x$ $ightarrow$ $+x$ $+x$

Equil. $9.99 \times 10^{-2} - x$ $x$ $x$

$$K_a = 6.4 \times 10^{-5} = \frac{[\text{H}^+][\text{Bz}^-]}{[\text{HBz}]} = \frac{x^2}{9.99 \times 10^{-2} - x} \approx \frac{x^2}{9.99 \times 10^{-2}} \quad \text{(assuming } x \ll 9.99 \times 10^{-2})$$

$$x = [\text{H}^+] = 2.5 \times 10^{-3} \, M; \quad \text{Assumptions good (} x \text{ is } 2.5\% \text{ of } 9.99 \times 10^{-2}).$$

So: $x = [\text{H}^+] = [\text{Bz}^-] = 2.5 \times 10^{-3} \, M; \quad [\text{HBz}] = 9.99 \times 10^{-2} - x = 9.74 \times 10^{-2} \, M$

$$\text{pH} = 2.60; \quad \text{pOH} = 11.40; \quad [\text{OH}^-] = 10^{-11.40} = 4.0 \times 10^{-12} \, M$$
60. Major species: HIO₃, H₂O; Major source of H⁺: HIO₃ (a weak acid, Kₐ = 0.17)

\[
\text{HIO}_3 \rightleftharpoons H^+ + IO_3^-
\]

Initial \(0.20 M\) \(-0\) \(0\)

\(x\) mol/L HIO₃ dissociates to reach equilibrium

Change \(-x\) \(\rightarrow\) \(+x\) \(+x\)

Equil. \(0.20 - x\) \(x\) \(x\)

\[K_a = 0.17 = \frac{[H^+][IO_3^-]}{[HIO_3]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}, \quad x = 0.18; \quad \text{Check assumption.}\]

Assumption is horrible (\(x\) is 90% of 0.20). When the assumption is this poor, it is generally quickest to solve exactly using the quadratic formula (see Appendix 1.4 in text). The method of successive approximations will require many trials to finally converge on the answer. For this problem, 5 trials were required. Using the quadratic formula and carrying extra significant figures:

\[0.17 = \frac{x^2}{0.20 - x}, \quad x^2 = 0.17(0.20 - x), \quad x^2 + 0.17x - 0.034 = 0\]

\[x = \frac{-0.17 \pm \sqrt{(0.17)^2 - 4(1)(-0.034)}}{2(1)} = \frac{-0.17 \pm 0.406}{2}, \quad x = 0.12 \text{ or } -0.29\]

Only \(x = 0.12\) makes sense. \(x = 0.12 M = [H^+]; \quad \text{pH} = -\log (0.12) = 0.92\)

64. HF and HOC₆H₅ are both weak acids with \(K_a\) values of \(7.2 \times 10^{-4}\) and \(1.6 \times 10^{-10}\), respectively. Since the \(K_a\) value for HF is much greater than the \(K_a\) value for HOC₆H₅, then HF will be the dominant producer of H⁺ (we can ignore the amount of H⁺ produced from HOC₆H₅ since it will be insignificant).

\[
\text{HF} \rightleftharpoons H^+ + F^-
\]

Initial \(0.10 M\) \(-0\) \(0\)

\(x\) mol/L HF dissociates to reach equilibrium

Change \(-x\) \(\rightarrow\) \(+x\) \(+x\)

Equil. \(0.10 - x\) \(x\) \(x\)

\[K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}\]

\[x = [H^+] = 2.7 \times 10^{-2} M; \quad \text{pH} = -\log (2.7 \times 10^{-2}) = 1.57 \quad \text{Assumptions good.}\]

Solving for \([\text{OC}_6\text{H}_5^-]\) using HOC₆H₅ = H⁺ + OC₆H₅⁻ equilibrium:

\[K_a = 1.6 \times 10^{-10} = \frac{[H^+][\text{OC}_6\text{H}_5^-]}{[\text{HOC}_6\text{H}_5]} = \frac{(2.7 \times 10^{-2})[\text{OC}_6\text{H}_5^-]}{1.0}, \quad [\text{OC}_6\text{H}_5^-] = 5.9 \times 10^{-9} M\]

Note that this answer indicates that only \(5.9 \times 10^{-9} M\) HOC₆H₅ dissociates which indicates that HF is truly the only significant producer of H⁺ in this solution.
In all parts of this problem, acetic acid (HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}) is the best weak acid present. We must solve a weak acid problem.

a. \[ \text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_5\text{O}_2^- \]

Initial \[ 0.50 \text{ M} \]
\[ \text{mol/L HC}_2\text{H}_3\text{O}_2 \text{ dissociates to reach equilibrium} \]
Change \[ -x \rightarrow +x \quad +x \]
Equil. \[ 0.50 - x \quad x \quad x \]

\[ K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} \]

\[ x = [\text{H}^+] = [\text{C}_2\text{H}_5\text{O}_2^-] = 3.0 \times 10^{-3} \text{ M} \quad \text{Assumptions good.} \]

\[ \text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times 100 = \frac{3.0 \times 10^{-3}}{0.50} \times 100 = 0.60\% \]

b. The set-up for solutions b and c are similar to solution a except the final equation is slightly different, reflecting the new concentration of HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}.

\[ K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} \]

\[ x = [\text{H}^+] = [\text{C}_2\text{H}_5\text{O}_2^-] = 9.5 \times 10^{-4} \text{ M} \quad \text{Assumptions good.} \]

\[ \% \text{ dissociation} = \frac{9.5 \times 10^{-4}}{0.050} \times 100 = 1.9\% \]

c. \[ K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.0050 - x} = \frac{x^2}{0.0050} \]

\[ x = [\text{H}^+] = [\text{C}_2\text{H}_5\text{O}_2^-] = 3.0 \times 10^{-4} \text{ M}; \quad \text{Check assumptions.} \]

Assumption that \( x \) is negligible is borderline (6.0\% error). We should solve exactly. Using the method of successive approximations (see Appendix 1.4 of text):

\[ 1.8 \times 10^{-5} = \frac{x^2}{0.0050 - 3.0 \times 10^{-4}} = \frac{x^2}{0.0047}, \quad x = 2.9 \times 10^{-4} \]

Next trial also gives \( x = 2.9 \times 10^{-4} \).

\[ \% \text{ dissociation} = \frac{2.9 \times 10^{-4}}{5.0 \times 10^{-3}} \times 100 = 5.8\% \]

d. As we dilute a solution, all concentrations are decreased. Dilution will shift the equilibrium to the side with the greater number of particles. For example, suppose we double the volume of an equilibrium mixture of a weak acid by adding water, then:

\[ Q = \left( \frac{[\text{H}^+]_{eq}}{2} \right) \left( \frac{[\text{X}^-]_{eq}}{2} \right) \left( \frac{[\text{HX}]_{eq}}{2} \right) = \frac{1}{2} K_a \]

\( Q < K_a \), so the equilibrium shifts to the right or towards a greater percent dissociation.

c. \([\text{H}^+]\) depends on the initial concentration of weak acid and on how much weak acid dissociates. For solutions a-c the initial concentration of acid decreases more rapidly than the percent dissociation increases. Thus, \([\text{H}^+]\) decreases.
Let HX symbolize the weak acid. Set-up the problem like a typical weak acid equilibrium problem.

\[
\begin{align*}
\text{HX} & \quad \rightleftharpoons \quad \text{H}^+ & + & \text{X}^- \\
\text{Initial} & \quad 0.15 & \quad \sim 0 & \quad 0 \\
& x \text{ mol/L HX dissociates to reach equilibrium} \\
\text{Change} & \quad -x & \quad \rightarrow & \quad +x & \quad +x \\
\text{Equil.} & \quad 0.15 - x & \quad x & \quad x \\
\end{align*}
\]

If the acid is 3.0% dissociated, then \( x = [\text{H}^+] \) is 3.0% of 0.15: \( x = 0.030 \times (0.15 \text{ M}) = 4.5 \times 10^{-3} \text{ M} \)

Now that we know the value of \( x \), we can solve for \( K_a \).

\[
K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = \frac{x^2}{0.15 - x} = \frac{(4.5 \times 10^{-3})^2}{0.15 - 4.5 \times 10^{-3}} = 1.4 \times 10^{-4}
\]