CHAPTER 16
ACIDS AND BASES

16.1 A Brønsted acid is a proton donor, and a Brønsted base is a proton acceptor. Arrhenius acids are substances that ionize in water to produce $\text{H}^+$ ions and Arrhenius bases are substances that ionize in water to produce $\text{OH}^{-}$ ions.

16.2 A Brønsted base is a hydrogen ion ($\text{H}^+$) acceptor. A hydrogen ion has no electrons, so in order to form a bond to $\text{H}^+$, two electrons (or a lone pair) must be supplied by the base.

16.3 Table 16.2 of the text contains a list of important Brønsted acids and bases. (a) both (why?), (b) base, (c) acid, (d) base, (e) acid, (f) base, (g) base, (h) base, (i) acid, (j) acid.

16.4 Recall that the conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid.

(a) nitrite ion: $\text{NO}_2^{-}$
(b) hydrogen sulfate ion (also called bisulfate ion): $\text{HSO}_4^{-}$
(c) hydrogen sulfide ion (also called bisulfide ion): $\text{HS}^{-}$
(d) cyanide ion: $\text{CN}^{-}$
(e) formate ion: $\text{HCOO}^{-}$

16.5 In general the components of the conjugate acid–base pair are on opposite sides of the reaction arrow. The base always has one fewer proton than the acid.

(a) The conjugate acid–base pairs are (1) HCN (acid) and CN$^{-}$ (base) and (2) CH$_3$COO$^{-}$ (base) and CH$_3$COOH (acid).
(b) (1) HCO$_3^{-}$ (acid) and CO$_3^{2-}$ (base) and (2) HCO$_3^{-}$ (base) and H$_2$CO$_3$ (acid).
(c) (1) H$_2$PO$_4^{-}$ (acid) and HPO$_4^{2-}$ (base) and (2) NH$_3$ (base) and NH$_4^{+}$ (acid).
(d) (1) HClO (acid) and ClO$^{-}$ (base) and (2) CH$_3$NH$_2$ (base) and CH$_3$NH$_3^{+}$ (acid).
(e) (1) H$_2$O (acid) and OH$^{-}$ (base) and (2) CO$_3^{2-}$ (base) and HCO$_3^{-}$ (acid).
(f) (1) H$_2$O (acid) and OH$^{-}$ (base) and (2) CH$_3$COO$^{-}$ (base) and CH$_3$COOH (acid).

16.6 The conjugate acid of any base is just the base with a proton added.

(a) H$_2$S    (b) H$_2$CO$_3$    (c) HCO$_3^{-}$    (d) H$_3$PO$_4$    (e) H$_2$PO$_4^{-}$
(f) HPO$_4^{2-}$    (g) H$_2$SO$_4$    (h) HSO$_4^{-}$    (i) HNO$_2$    (j) HSO$_3^{-}$

16.7 The conjugate base of any acid is simply the acid minus one proton.

(a) CH$_2$CICO$^-_O$    (b) $\text{IO}_4^{-}$    (c) H$_2$PO$_4^{-}$    (d) HPO$_4^{2-}$    (e) PO$_4^{3-}$
(f) HSO$_4^{-}$    (g) SO$_4^{2-}$    (h) HCOO$^{-}$    (i) SO$_3^{2-}$    (j) NH$_3$
(k) HS$^{-}$    (l) $S^{2-}$    (m) ClO$^{-}$
16.8 (a) The Lewis structures are

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4 & : \\
\text{C} & \equiv \text{C} \quad \text{and} \quad \text{O} \equiv \text{C} \quad \text{O} \\
\text{O}^{-} & \quad \text{and} \quad \text{O}^{-} \\
\text{O}^{-} & \quad \text{O}^{-} \\
\text{C} & \equiv \text{C} \\
\text{O}^{-} & \quad \text{H} \\
\text{O}^{-} & \quad \text{O}^{-}
\end{align*}
\]

(b) \(H^+\) and \(H_2C_2O_4\) can act only as acids, \(HC_2O_4^-\) can act as both an acid and a base, and \(C_2O_4^{2-}\) can act only as a base.

16.9 \(K_w\) is called the ion-product constant, which is the product of the molar concentrations of \(H^+\) and \(OH^-\) ions at a particular temperature \((K_w = [H^+] [OH^-])\).

16.10 \(K_w = 1.0 \times 10^{-14} = [H^+] [OH^-]\)

16.11 Because the equilibrium constant increases as the temperature is raised, the process is endothermic.

16.12 pH is the negative logarithm of the hydrogen ion concentration. The concentrations of \(H^+\) and \(OH^-\) ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with. Taking the negative logarithm of the hydrogen ion concentration gives numbers typically in the range of 0 – 14.

16.13 No. You would need to know the temperature and the ion-product constant of water at that temperature. The pH of a solution can be zero or negative. At 25°C, a 1 \(M\) aqueous solution of HCl, assuming complete ionization, has a pH of zero.

16.14 pOH is the negative logarithm of the hydroxide concentration. \(pH + pOH = 14\) at 25°C.

16.15 Since \(pH = -\log[H^+]\), we write \([H^+] = 10^{-pH}\)

\[
\begin{align*}
\text{(a)} & & \quad [H^+] = 10^{-2.42} = 3.8 \times 10^{-3} \text{ M} & & \quad \text{(c)} & & \quad [H^+] = 10^{-6.96} = 1.1 \times 10^{-7} \text{ M} \\
\text{(b)} & & \quad [H^+] = 10^{-11.21} = 6.2 \times 10^{-12} \text{ M} & & \quad \text{(d)} & & \quad [H^+] = 10^{-15.00} = 1.0 \times 10^{-15} \text{ M}
\end{align*}
\]

16.16 **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, \([H^+] = 10^{-pH}\).

**Solution:** From Equation (16.5) of the text:

\[
\begin{align*}
\text{(a)} & & & & \quad \text{pH} = -\log[H^+] = 5.20 \\
& & & & \quad \log[H^+] = -5.20 \\
& & & & \quad \text{To calculate } [H^+], \text{ we need to take the antilog of } -5.20. \\
& & & & \quad [H^+] = 10^{-5.20} = 6.3 \times 10^{-6} \text{ M}
\end{align*}
\]

**Check:** Because the pH is between 5 and 6, we can expect \([H^+]\) to be between \(1 \times 10^{-5} \text{ M}\) and \(1 \times 10^{-6} \text{ M}\). Therefore, the answer is reasonable.
(b)  \[ \text{pH} = -\log [H^+] = 16.00 \]
\[ \log[H^+] = -16.00 \]
\[ [H^+] = 10^{-16.00} = 1.0 \times 10^{-16} M \]

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

**Solution:** The ion product of water is applicable to all aqueous solutions. At 25\(^\circ\)C,
\[ K_w = 1.0 \times 10^{-14} = [H^+][\text{OH}^-] \]
Rearranging the equation to solve for \([H^+]\), we write
\[ [H^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-9}} = 2.7 \times 10^{-6} M \]

**Check:** Since the \([\text{OH}^-] < 1 \times 10^{-7} M\) we expect the \([H^+]\) to be greater than \(1 \times 10^{-7} M\).

16.17 (a) HCl is a strong acid, so the concentration of hydrogen ion is also 0.0010 \(M\). (What is the concentration of chloride ion?) We use the definition of pH.
\[ \text{pH} = -\log[H^+] = -\log(0.0010) = 3.00 \]

(b) KOH is an ionic compound (why?) and is fully ionized. We first find the concentration of hydrogen ion.
\[ [H^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.76} = 1.3 \times 10^{-14} M \]

The pH is then found from its defining equation
\[ \text{pH} = -\log[H^+] = -\log[1.3 \times 10^{-14}] = 13.89 \]

(c) Ba(OH)\(_2\) is ionic and fully ionized in water. The concentration of the hydroxide ion is \(5.6 \times 10^{-4} M\) (Why? What is the concentration of Ba\(^{2+}\)?) We find the hydrogen ion concentration.
\[ [H^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11} M \]

The pH is then:
\[ \text{pH} = -\log[H^+] = -\log(1.8 \times 10^{-11}) = 10.74 \]

(d) Nitric acid is a strong acid, so the concentration of hydrogen ion is also \(5.2 \times 10^{-4} M\). The pH is:
\[ \text{pH} = -\log[H^+] = -\log(5.2 \times 10^{-4}) = 3.28 \]

16.18 The ion product for water is applicable to all aqueous solutions. However, at 40\(^\circ\)C, \(K_w\) has a larger value.
\[ K_w = 3.8 \times 10^{-14} = [H^+] [\text{OH}^-] \]
The mole ratio of $H^+$ to $OH^-$ is 1:1 for the autoionization of water. Let $x$ equal the $H^+$ concentration.

\[ 3.8 \times 10^{-14} = x^2 \]

\[ x = [H^+] = 1.9 \times 10^{-7} \, M \]

\[ pH = -\log[H^+] = -\log(1.9 \times 10^{-7}) = 6.72 \]

Is this water sample neutral?

<table>
<thead>
<tr>
<th>$\text{pH}$</th>
<th>$[H^+]$</th>
<th>Solution is:</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 7</td>
<td>&gt; $1.0 \times 10^{-7} , M$</td>
<td>acid</td>
</tr>
<tr>
<td>&gt; 7</td>
<td>&lt; $1.0 \times 10^{-7} , M$</td>
<td>basic</td>
</tr>
<tr>
<td>= 7</td>
<td>= $1.0 \times 10^{-7} , M$</td>
<td>neutral</td>
</tr>
</tbody>
</table>

16.19

(a) acidic  (b) neutral  (c) basic

16.20

The $pH$ can be found by using Equation (16.10) of the text.

\[ pH = 14.00 - pOH = 14.00 - 9.40 = 4.60 \]

The hydrogen ion concentration can be found as in Example 16.4 of the text.

\[ 4.60 = -\log[H^+] \]

Taking the antilog of both sides:

\[ [H^+] = 2.5 \times 10^{-5} \, M \]

16.21

\[ 5.50 \, \text{mL} \times \frac{1 \, \text{L}}{1000 \, \text{mL}} \times \frac{0.360 \, \text{mol}}{1 \, \text{L}} = 1.98 \times 10^{-3} \, \text{mol KOH} \]

KOH is a strong base and therefore ionizes completely. The $OH^-$ concentration equals the KOH concentration, because there is a 1:1 mole ratio between KOH and $OH^-$.  

\[ [OH^-] = 0.360 \, M \]

\[ pOH = -\log[OH^-] = 0.444 \]

16.22

\[ \text{Molarity of the HCl solution is:} \quad \frac{18.4 \, \text{g HCl}}{36.46 \, \text{g HCl}} \times \frac{1 \, \text{mol HCl}}{662 \times 10^{-3} \, \text{L}} = 0.762 \, M \]

\[ pH = -\log(0.762) = 0.118 \]

16.23

We can calculate the $OH^-$ concentration from the pOH.

\[ pOH = 14.00 - pH = 14.00 - 10.00 = 4.00 \]

\[ [OH^-] = 10^{-pOH} = 1.0 \times 10^{-4} \, M \]
Since NaOH is a strong base, it ionizes completely. The OH\(^-\) concentration equals the initial concentration of NaOH.

\[
[NaOH] = 1.0 \times 10^{-4} \text{ mol/L}
\]

So, we need to prepare 546 mL of 1.0 \times 10^{-4} M NaOH.

This is a dimensional analysis problem. We need to perform the following unit conversions.

\[
\text{mol/L} \rightarrow \text{mol NaOH} \rightarrow \text{grams NaOH}
\]

\[
\text{? g NaOH} = 546 \text{ mL} \times \frac{1.0 \times 10^{-4} \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} = 2.2 \times 10^{-3} \text{ g NaOH}
\]

16.25 The strength of an acid or base is determined by the extent of ionization in water. Strong acids and strong bases are strong electrolytes which, for practical purposes, are assumed to ionize completely in water. Weak acids and weak bases are weak electrolytes, which ionize only to a limited extent in water.

16.26 Strong acids: HCl, HBr, H\(_2\)SO\(_4\), HNO\(_3\).
Weak acids: HF, HNO\(_2\), CH\(_3\)COOH, C\(_6\)H\(_5\)COOH

16.27 The strongest acid that can exist in water is the hydronium ion, H\(_3\)O\(^+\), and the strongest base that can exist in water is the hydroxide ion, OH\(^-\).

16.28 HSO\(_4^-\) is the conjugate base of the strong acid H\(_2\)SO\(_4\), and therefore has negligible base strength in water. It does, however, have an H\(^+\) that it could donate. In fact HSO\(_4^-\) is a weak acid. For a polyprotic acid, the first ionization constant is much larger than the second ionization constant, and so on because it becomes harder to remove another H\(^+\) ion from a negatively charged ion.

16.29 A strong acid, such as HCl, will be completely ionized, choice (b).
A weak acid will only ionize to a lesser extent compared to a strong acid, choice (e).
A very weak acid will remain almost exclusively as the acid molecule in solution. Choice (d) is the best choice.

16.30 (1) The two steps in the ionization of a weak diprotic acid are:

\[
\begin{align*}
\text{H}_2\text{A}(aq) + \text{H}_2\text{O}(l) \rightarrow & \text{ H}_2\text{O}^+ (aq) + \text{HA}^- (aq) \\
\text{HA}^- (aq) + \text{H}_2\text{O}(l) \rightarrow & \text{ H}_2\text{O}^+ (aq) + \text{A}^{2-} (aq)
\end{align*}
\]

The diagram that represents a weak diprotic acid is (c). In this diagram, we only see the first step of the ionization, because HA\(^-\) is a much weaker acid than H\(_2\)A.

(2) Both (b) and (d) are chemically implausible situations. Because HA\(^-\) is a much weaker acid than H\(_2\)A, you would not see a higher concentration of A\(^{2-}\) compared to HA\(^-\).

16.31 (a) strong acid, (b) weak acid, (c) strong acid (first stage of ionization),
(d) weak acid, (e) weak acid, (f) weak acid,
(g) strong acid, (h) weak acid, (i) weak acid.
16.32  (a) strong base  (b) weak base  (c) weak base  (d) weak base  (e) strong base

16.33  The maximum possible concentration of hydrogen ion in a 0.10 M solution of HA is 0.10 M. This is the case if HA is a strong acid. If HA is a weak acid, the hydrogen ion concentration is less than 0.10 M. The pH corresponding to 0.10 M [H$^+$] is 1.00. (Why three digits?) For a smaller [H$^+$] the pH is larger than 1.00 (why?).

(a) false, the pH is greater than 1.00;  (b) false, they are equal;  (c) true,  (d) false.

16.34  (a) false, they are equal  (b) true, find the value of log(1.00) on your calculator  (c) true  (d) false.

16.35  The direction should favor formation of F$^-$ (aq) and H$_2$O(l). Hydroxide ion is a stronger base than fluoride ion, and hydrofluoric acid is a stronger acid than water.

16.36  Cl$^-$ is the conjugate base of the strong acid, HCl. It is a negligibly weak base and has no affinity for protons. Therefore, the reaction will not proceed from left to right to any measurable extent.

Another way to think about this problem is to consider the possible products of the reaction.

\[
\text{CH}_3\text{COOH(aq)} + \text{Cl}^- (aq) \rightarrow \text{HCl(aq)} + \text{CH}_3\text{COO}^- (aq)
\]

The favored reaction is the one that proceeds from right to left. HCl is a strong acid and will ionize completely, donating all its protons to the base, CH$_3$COO$^-$. 

16.37  The larger the value of $K_a$, the stronger the acid—that is, the greater the concentration of H$^+$ ions at equilibrium due to its ionization.

16.38  $K_a$ depends on the temperature and the structure of the weak acid.

16.39  The $K_a$ values of strong acids are so large that we assume strong acids ionize completely in water. Also, the $K_a$ values of strong acids are difficult to determine accurately. The value of an equilibrium constant, in this case $K_a$, changes with temperature; therefore, it is necessary to specify temperature when giving $K_a$ values.

16.40  HCOOH and CH$_3$COOH are weak acids. The $K_a$ value of CH$_3$COOH is smaller than the $K_a$ for HCOOH, and therefore CH$_3$COOH is the weaker acid and will have the highest pH of the solutions at a given concentration.

16.41  HCN is a weak acid. Setting up the equilibrium:

\[
\begin{array}{ccc}
\text{Initial (M)} & 0.15 & 0 & 0 \\
\text{Change (M)} & -x & +x & +x \\
\text{Equilibrium (M)} & 0.15 - x & x & x \\
\end{array}
\]

\[
K_a = \frac{[H^+][CN^-]}{[HCN]}
\]
You can look up the $K_a$ value for HCN in Table 16.3 of the text.

$$4.9 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Make the assumption that $0.15 - x \approx 0.15$ due to the very small value of $K_a$.

$$4.9 \times 10^{-10} \approx \frac{x^2}{0.15}$$

$x = [H^+] = [CN^-] = 8.6 \times 10^{-6} \text{ M}$

$[HCN] = 0.15 - x = 0.15 \text{ M}$

$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{8.6 \times 10^{-6}} = 1.2 \times 10^{-9} \text{ M}$

**16.42 Strategy:** Recall that a weak acid only partially ionizes in water. We are given the initial quantity of a weak acid (CH$_3$COOH) and asked to calculate the concentrations of H$^+$, CH$_3$COO$^-$, and CH$_3$COOH at equilibrium. First, we need to calculate the initial concentration of CH$_3$COOH. In determining the H$^+$ concentration, we ignore the ionization of H$_2$O as a source of H$^+$, so the major source of H$^+$ ions is the acid. We follow the procedure outlined in Section 16.5 of the text.

**Solution:**

**Step 1:** Calculate the concentration of acetic acid before ionization.

$$\frac{0.0560 \text{ g acetic acid}}{60.05 \text{ g acetic acid}} \times \frac{1 \text{ mol acetic acid}}{\text{ mol}} = 9.33 \times 10^{-4} \text{ mol acetic acid}$$

$$\frac{9.33 \times 10^{-4} \text{ mol}}{0.0500 \text{ L soln}} = 0.0187 \text{ M acetic acid}$$

**Step 2:** We ignore water’s contribution to [H$^+$]. We consider CH$_3$COOH as the only source of H$^+$ ions.

**Step 3:** Letting $x$ be the equilibrium contribution of H$^+$ and CH$_3$COO$^-$ ions in mol/L, we summarize:

<table>
<thead>
<tr>
<th>Initial (M):</th>
<th>0.0187</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M):</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium (M):</td>
<td>0.0187 - $x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

**Step 3:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant ($K_a$), solve for $x$. You can look up the $K_a$ value in Table 16.3 of the text.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.0187 - x)}$$
At this point, we can make an assumption that $x$ is very small compared to 0.0187. Hence,

$$0.0187 - x \approx 0.0187$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.0187}$$

$$x = 5.8 \times 10^{-4} M = [H^+] = [CH_3COO^-]$$

$$[CH_3COOH] = (0.0187 - 5.8 \times 10^{-4})M = 0.0181 M$$

**Check:** Testing the validity of the assumption,

$$\frac{5.8 \times 10^{-4}}{0.0187} \times 100\% = 3.1\% < 5\%$$

The assumption is valid.

16.43 First we find the hydrogen ion concentration.

$$[H^+] = 10^{-pH} = 10^{-6.20} = 6.3 \times 10^{-7} M$$

Substituting into the acid ionization constant expression:

$$K_a = 7.1 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(6.3 \times 10^{-7})[F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = 1.1 \times 10^3$$

We have omitted the contribution to $[H^+]$ due to water.

16.44 A pH of 3.26 corresponds to a $[H^+]$ of $5.5 \times 10^{-4} M$. Let the original concentration of formic acid be $I$. If the concentration of $[H^+]$ is $5.5 \times 10^{-4} M$, that means that $5.5 \times 10^{-4} M$ of HCOOH ionized because of the 1:1 mole ratio between HCOOH and $H^+$.

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>HCOOH(aq)</th>
<th>$\dot{c}$</th>
<th>$H^+(aq)$</th>
<th>+</th>
<th>HCOO$^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>$-5.5 \times 10^{-4}$</td>
<td>$0$</td>
<td>$+5.5 \times 10^{-4}$</td>
<td>$+5.5 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>$I - (5.5 \times 10^{-4})$</td>
<td>$5.5 \times 10^{-4}$</td>
<td>$5.5 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Substitute $K_a$ and the equilibrium concentrations into the ionization constant expression to solve for $I$.

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

$$1.7 \times 10^{-4} = \frac{(5.5 \times 10^{-4})^2}{x - (5.5 \times 10^{-4})}$$

$$I = [HCOOH] = 2.3 \times 10^{-3} M$$
16.45 HF is a weak acid. Setting up the equilibrium:

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

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.060</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>0.060 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} 
\]

You can look up the \(K_a\) value for HF in Table 16.3 of the text.

\[
7.1 \times 10^{-4} = \frac{x^2}{0.060 - x}
\]

In this case, the assumption that \(0.060 - x \approx 0.060\) will not work. Solve a quadratic equation.

\[
x^2 + (7.1 \times 10^{-4})x - (4.26 \times 10^{-5}) = 0
\]

\[
x = \frac{-7.1 \times 10^{-4} \pm \sqrt{(7.1 \times 10^{-4})^2 - 4(1)(-4.26 \times 10^{-5})}}{2(1)}
\]

\[
x = 6.2 \times 10^{-3} \text{ M} \quad \text{or} \quad x = -6.9 \times 10^{-3} \text{ M}
\]

The second solution is physically impossible, because the concentrations of ions produced as a result of the weak acid ionization cannot be negative. The positive root is the correct solution.

\[
\text{pH} = -\log[\text{H}^+] = -\log(6.2 \times 10^{-3}) = 2.21
\]

16.46 Percent ionization is defined as:

\[
\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\%
\]

For a monoprotic acid, HA, the concentration of acid that undergoes ionization is equal to the concentration of \(\text{H}^+\) ions or the concentration of \(\text{A}^-\) ions at equilibrium. Thus, we can write:

\[
\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%
\]

(a) First, recognize that hydrofluoric acid is a weak acid. It is not one of the six strong acids, so it must be a weak acid.

Step 1: Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown \(x\), that represents the change in concentration. Let \((-x)\) be the depletion in concentration (mol/L) of HF. From the stoichiometry of the reaction, it follows that the increase in concentration for both \(\text{H}^+\) and \(\text{F}^-\) must be \(x\). Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

<table>
<thead>
<tr>
<th>Initial (M):</th>
<th>0.60</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M):</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium (M):</td>
<td>0.60 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
**Step 2:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant \( K_a \), solve for \( x \).

\[
K_a = \frac{[H^+][F^-]}{[HF]}
\]

You can look up the \( K_a \) value for hydrofluoric acid in Table 16.3 of your text.

\[
7.1 \times 10^{-4} = \frac{(x)(x)}{(0.60 - x)}
\]

At this point, we can make an assumption that \( x \) is very small compared to 0.60. Hence,

\[
0.60 - x \approx 0.60
\]

Oftentimes, assumptions such as these are valid if \( K \) is very small. A very small value of \( K \) means that a very small amount of reactants go to products. Hence, \( x \) is small. If we did not make this assumption, we would have to solve a quadratic equation.

\[
7.1 \times 10^{-4} = \frac{(x)(x)}{0.60}
\]

Solving for \( x \).

\[
x = 0.021 M = [H^+]
\]

**Step 3:** Having solved for the \([H^+]\), calculate the percent ionization.

\[
\text{percent ionization} = \frac{[H^+]}{[HF]_0} \times 100\% = \frac{0.021 M}{0.60 M} \times 100\% = 3.5\%
\]

(b) – (d) are worked in a similar manner to part (a). However, as the initial concentration of HF becomes smaller, the assumption that \( x \) is very small compared to this concentration will no longer be valid. You must solve a quadratic equation.

(b) \( K_a = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{(0.080 - x)} = 7.1 \times 10^{-4} \)

\[
x^2 + (7.1 \times 10^{-4})x - (5.7 \times 10^{-5}) = 0
\]

\[
x = 7.2 \times 10^{-3} M
\]

**Percent ionization** = \( \frac{7.2 \times 10^{-3} M}{0.080 M} \times 100\% = 9.0\% \)

(c) \( K_a = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{(0.0046 - x)} = 7.1 \times 10^{-4} \)

\[
x^2 + (7.1 \times 10^{-4})x - (3.3 \times 10^{-6}) = 0
\]

\[
x = 1.5 \times 10^{-3} M
\]

**Percent ionization** = \( \frac{1.5 \times 10^{-3} M}{0.0046 M} \times 100\% = 33\% \)
(d) \( K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{(0.00028 - x)} = 7.1 \times 10^{-4} \)

\[x^2 + (7.1 \times 10^{-4})x - (2.0 \times 10^{-7}) = 0\]

\(x = 2.2 \times 10^{-4} \text{ M}\)

Percent ionization = \(\frac{2.2 \times 10^{-4} \text{ M}}{0.00028 \text{ M}} \times 100\% = 79\%\)

As the solution becomes more dilute, the percent ionization increases.

16.47 Given 14% ionization, the concentrations must be:

\[[\text{H}^+] = [\text{A}^-] = 0.14 \times 0.040 \text{ M} = 0.0056 \text{ M}\]

\[[\text{HA}] = (0.040 - 0.0056) \text{ M} = 0.034 \text{ M}\]

The value of \(K_a\) can be found by substitution.

\[K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.0056)^2}{0.034} = 9.2 \times 10^{-4} \]

16.48 The equilibrium is:

\[\text{C}_9\text{H}_8\text{O}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_9\text{H}_7\text{O}_4^-(\text{aq})\]

| Initial (M) | 0.20 | 0 | 0 |
| Change (M) | \(-x\) | +x | +x |
| Equilibrium (M) | 0.20 - x | x | x |

(a) \( K_a = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{C}_9\text{H}_8\text{O}_4^-]}\)

\[3.0 \times 10^{-4} = \frac{x^2}{(0.20 - x)}\]

Assuming \(0.20 - x \approx 0.20\)

\(x = [\text{H}^+] = 7.7 \times 10^{-3} \text{ M}\)

Percent ionization = \(\frac{x}{0.20} \times 100\% = \frac{7.7 \times 10^{-3} \text{ M}}{0.20 \text{ M}} \times 100\% = 3.9\%\)

(b) At pH 1.00 the concentration of hydrogen ion is 0.10 M ([H\(^+\)] = 10\(^{-pH}\)). The extra hydrogen ions will tend to suppress the ionization of the weak acid (LeChâtelier's principle, Section 15.4 of the text). The position of equilibrium is shifted in the direction of the un-ionized acid. Let's set up a table of concentrations with the initial concentration of H\(^+\) equal to 0.10 M.

| Initial (M) | 0.20 | 0.10 | 0 |
| Change (M) | \(-x\) | +x | +x |
| Equilibrium (M) | 0.20 - x | 0.10 + x | x |
CHAPTER 16: ACIDS AND BASES

16.49 A diprotic acid has two hydrogen ions that can be donated per molecule. These acids 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.

16.50 Brønsted acid: \(H_3PO_4\), \(H_2PO_4^-\), \(HPO_4^{2-}\), \(H_3O^+\)
Brønsted base: \(H_2PO_4^-\), \(HPO_4^{2-}\), \(PO_4^{3-}\), \(OH^-\)
Both acid and base: \(H_2PO_4^-\), \(HPO_4^{2-}\)

16.51 There is no \(H_2SO_4\) in the solution because \(HSO_4^-\) has no tendency to accept a proton to produce \(H_2SO_4\). (Why?) We are only concerned with the ionization

\[
\begin{align*}
\text{Initial (M):} & \quad 0.20 & 0.00 & 0.00 \\
\text{Change (M):} & \quad -x & +x & +x \\
\text{Equilibrium (M):} & \quad (0.20 - x) & +x & +x
\end{align*}
\]

\[
K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}
\]

\[
1.3 \times 10^{-2} = \frac{(x)(x)}{(0.20 - x)}
\]

Solving the quadratic equation:

\[
x = [H^+] = [SO_4^{2-}] = 0.045 \text{ M}
\]

\[
[HSO_4^-] = (0.20 - 0.045) \text{ M} = 0.16 \text{ M}
\]

16.52 For the first stage of ionization:

\[
\begin{align*}
\text{Initial (M):} & \quad 0.025 & 0.00 & 0.00 \\
\text{Change (M):} & \quad -x & +x & +x \\
\text{Equilibrium (M):} & \quad (0.025 - x) & x & x
\end{align*}
\]
\[ K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \]

\[ 4.2 \times 10^{-7} = \frac{x^2}{(0.025 - x)} \approx \frac{x^2}{0.025} \]

\[ x = 1.0 \times 10^{-4} \text{ M} \]

For the second ionization,

\[ \text{HCO}_3^- (aq) \xrightarrow{\text{H}^+} \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \]

Initial (M):

\[ 1.0 \times 10^{-4} \quad 1.0 \times 10^{-4} \quad 0.00 \]

Change (M):

\[ -x \quad +x \quad +x \]

Equilibrium (M):

\[ (1.0 \times 10^{-4}) - x \quad (1.0 \times 10^{-4}) + x \quad x \]

\[ K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \]

\[ 4.8 \times 10^{-11} = \frac{(1.0 \times 10^{-4} + x)(x)}{(1.0 \times 10^{-4} - x)} = \frac{(1.0 \times 10^{-4})(x)}{(1.0 \times 10^{-4})} \]

\[ x = 4.8 \times 10^{-11} \text{ M} \]

Since \text{HCO}_3^- is a very weak acid, there is little ionization at this stage. Therefore we have:

\[ [\text{H}^+] = [\text{HCO}_3^-] = 1.0 \times 10^{-4} \text{ M and } [\text{CO}_3^{2-}] = x = 4.8 \times 10^{-11} \text{ M} \]  

16.53 Weak bases are weak electrolytes, which ionize only to a limited extent in water. In water, ammonia partially ionizes to produce hydroxide ions: \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq). The ionization constant \( (K_b) \) for this reaction at 25°C is \( 1.8 \times 10^{-5} \). The small value of the ionization constant indicates that this equilibrium lies to the left and only a small amount of hydroxide ions are produced in solution.

16.54 \( K_w = K_a \times K_b. \)

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \quad K_b \]

\[ \text{NH}_4^+(aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}^+(aq) \quad K_a \]

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad K_w \]

When two reactions are added to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions.

16.55 (a) We construct the usual table.

\[
\begin{array}{ccc}
\text{NH}_3(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{NH}_4^+(aq) + \text{OH}^-(aq) \\
\text{Initial (M):} & 0.10 & 0.00 & 0.00 \\
\text{Change (M):} & -x & +x & +x \\
\text{Equilibrium (M):} & (0.10 - x) & x & x \\
\end{array}
\]
\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

\[ 1.8 \times 10^{-5} = \frac{x^2}{(0.10 - x)} \]

Assuming \((0.10 - x) \approx 0.10\), we have:

\[ 1.8 \times 10^{-5} = \frac{x^2}{0.10} \]

\[ x = 1.3 \times 10^{-3} \text{ M} = [\text{OH}^-] \]

\[ \text{pOH} = -\log(1.3 \times 10^{-3}) = 2.89 \]

\[ \text{pH} = 14.00 - 2.89 = 11.11 \]

By following the identical procedure, we can show: \((b) \text{ pH} = 8.96\).

**16.56 Strategy:** Weak bases only partially ionize in water.

\[ \text{B(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq) \]

Note that the concentration of the weak base given refers to the initial concentration before ionization has started. The pH of the solution, on the other hand, refers to the situation at equilibrium. To calculate \(K_b\), we need to know the concentrations of all three species, \([\text{B}]\), \([\text{BH}^+]\), and \([\text{OH}^-]\) at equilibrium. We ignore the ionization of water as a source of \(\text{OH}^-\) ions.

**Solution:** We proceed as follows.

**Step 1:** The major species in solution are \(\text{B}, \text{OH}^-,\) and the conjugate acid \(\text{BH}^+\).

**Step 2:** First, we need to calculate the hydroxide ion concentration from the pH value. Calculate the pOH from the pH. Then, calculate the \(\text{OH}^-\) concentration from the pOH.

\[ \text{pOH} = 14.00 - \text{pH} = 14.00 - 10.66 = 3.34 \]

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

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

Taking the antilog of both sides of the equation,

\[ 10^{-\text{pOH}} = [\text{OH}^-] \]

\[ [\text{OH}^-] = 10^{-3.34} = 4.6 \times 10^{-4} \text{ M} \]

**Step 3:** If the concentration of \(\text{OH}^-\) is \(4.6 \times 10^{-4} \text{ M}\) at equilibrium, that must mean that \(4.6 \times 10^{-4} \text{ M}\) of the base ionized. We summarize the changes.

<table>
<thead>
<tr>
<th>Initial (M):</th>
<th>B(aq)</th>
<th>H(_2)O(l)</th>
<th>BH(^+(aq))</th>
<th>OH(^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M):</td>
<td>(-4.6 \times 10^{-4})</td>
<td>(0)</td>
<td>(+4.6 \times 10^{-4})</td>
<td>(+4.6 \times 10^{-4})</td>
</tr>
<tr>
<td>Equilibrium (M):</td>
<td>(0.30 - (4.6 \times 10^{-4}))</td>
<td>(4.6 \times 10^{-4})</td>
<td>(4.6 \times 10^{-4})</td>
<td></td>
</tr>
</tbody>
</table>
Step 4: Substitute the equilibrium concentrations into the ionization constant expression to solve for $K_b$.

\[
K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(4.6 \times 10^{-4})^2}{0.30 - (4.6 \times 10^{-4})} = 7.1 \times 10^{-7}
\]

A pH of 11.22 corresponds to a $[H^+]$ of $6.03 \times 10^{-12}$ M and a $[OH^-]$ of $1.66 \times 10^{-3}$ M.

Setting up a table:

<table>
<thead>
<tr>
<th></th>
<th>$\text{NH}_3(aq)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\text{NH}_4^+(aq)$</th>
<th>$\text{OH}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$I$</td>
<td>$0.00$</td>
<td>$0.00$</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-1.66 \times 10^{-3}$</td>
<td>$+1.66 \times 10^{-3}$</td>
<td>$+1.66 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$I - (1.66 \times 10^{-3})$</td>
<td>$1.66 \times 10^{-3}$</td>
<td>$1.66 \times 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{1.66 \times 10^{-3} \times 1.66 \times 10^{-3}}{I - (1.66 \times 10^{-3})} = 1.8 \times 10^{-5}
\]

Assuming $1.66 \times 10^{-3}$ is small relative to $I$, then

\[
I = 0.15 \text{ M} = [\text{NH}_3]
\]

The reaction is:

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

Initial (M):

<table>
<thead>
<tr>
<th></th>
<th>$\text{NH}_3(aq)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\text{NH}_4^+(aq)$</th>
<th>$\text{OH}^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$0.080$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$0.080 - x$</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

At equilibrium we have:

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.080 - x)} \approx \frac{x^2}{0.080}
\]

\[
x = 1.2 \times 10^{-3} \text{ M}
\]

\[
\text{Percent NH}_3 \text{ present as } \text{NH}_4^+ = \frac{1.2 \times 10^{-3}}{0.080} \times 100\% = 1.5\%
\]

Bond strength, bond polarity, properties of the solvent, and temperature.

The greater the electronegativity or the greater the oxidation number of the central atom, the stronger the oxoacid.
16.61 The strength of the $\text{H}^-\text{X}$ bond is the dominant factor in determining the strengths of binary acids. As with the hydrogen halides (see Section 16.8 of the text), the $\text{H}^-\text{X}$ bond strength decreases going down the column in Group 6A. The compound with the weakest $\text{H}^-\text{X}$ bond will be the strongest binary acid: $\text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$.

16.62 All the listed pairs are oxoacids that contain different central atoms whose elements are in the same group of the periodic table and have the same oxidation number. In this situation the acid with the most electronegative central atom will be the strongest.

(a) $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4$.

(b) $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4$

16.63 The $\text{CHCl}_2\text{COOH}$ is a stronger acid than $\text{CH}_2\text{ClCOOH}$. Having two electronegative chlorine atoms compared to one, will draw more electron density toward itself, making the $\text{O}^-\text{H}$ bond more polar. The hydrogen atom in $\text{CHCl}_2\text{COOH}$ is more easily ionized compared to the hydrogen atom in $\text{CH}_2\text{ClCOOH}$.

16.64 The conjugate bases are $\text{C}_6\text{H}_5\text{O}^-$ from phenol and $\text{CH}_3\text{O}^-$ from methanol. The $\text{C}_6\text{H}_5\text{O}^-$ is stabilized by resonance:

\[
\text{O}^- \quad \text{O} \quad \text{O} \quad \text{O}
\]

The $\text{CH}_3\text{O}^-$ ion has no such resonance stabilization. A more stable conjugate base means an increase in the strength of the acid.

16.65 Salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water. Depending on the salt, salt solutions can be acidic, basic, or neutral. See Section 16.9 of the text.

16.66 For hydrated metal ions, the extent of hydrolysis is greatest for the smallest and most highly charged ions because a “compact” highly charged ion is more effective in polarizing the $\text{O}^-\text{H}$ bond and facilitating ionization. See Figure 16.7 of the text.

16.67 $\text{Al}^{3+}$ does not have a hydrogen ion that it can donate, but $\text{Al(H}_2\text{O)}^{3+}_6$ does. In water, $\text{Al}^{3+}$ takes the hydrated form. A hydrogen ion from one of the water molecules can be donated; hence, $\text{Al(H}_2\text{O)}^{3+}_6$ functions as a Brønsted acid.

16.68 $\text{KF, NH}_4\text{NO}_2, \text{MgSO}_4, \text{KCN, C}_6\text{H}_5\text{COONa, Na}_2\text{CO}_3, \text{and HCOOK}$.

16.69 (a) pH $\approx 7$, (b) pH $< 7$, (c) pH $\approx 7$, (d) pH $< 7$

16.70 Be$^{2+}$ because it is the most compact, highly-charged ion of the group.
16.71 There are two possibilities: (i) MX is the salt of a strong acid and a strong base so that neither the cation nor the anion react with water to alter the pH and (ii) MX is the salt of a weak acid and a weak base with $K_a$ for the acid equal to $K_b$ for the base. The hydrolysis of one would be exactly offset by the hydrolysis of the other.

16.72 There is an inverse relationship between acid strength and conjugate base strength. As acid strength decreases, the proton accepting power of the conjugate base increases. In general the weaker the acid, the stronger the conjugate base. All three of the potassium salts ionize completely to form the conjugate base of the respective acid. The greater the pH, the stronger the conjugate base, and therefore, the weaker the acid. The order of increasing acid strength is $HZ < HY < HX$.

16.73 The salt sodium acetate completely dissociates upon dissolution, producing 0.36 M $[Na^+]$ and 0.36 M $[CH_3COO^-]$ ions. The $[CH_3COO^-]$ ions will undergo hydrolysis because they are a weak base.

\[
\text{CH}_3\text{COO}^- (aq) + H_2O(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^- (aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>$-x$</td>
<td>$(0.36 - x)$</td>
</tr>
<tr>
<td>0.00</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>$+x$</td>
</tr>
</tbody>
</table>

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

\[
5.6 \times 10^{-10} = \frac{x^2}{(0.36 - x)}
\]

Assuming $(0.36 - x) \approx 0.36$, then

\[
x = [\text{OH}^-] = 1.4 \times 10^{-5}
\]

\[
p\text{OH} = -\log(1.4 \times 10^{-5}) = 4.85
\]

\[
\text{pH} = 14.00 - 4.85 = 9.15
\]

16.74 The salt ammonium chloride completely ionizes upon dissolution, producing 0.42 M $[NH_4^+]$ and 0.42 M $[Cl^-]$ ions. $NH_4^+$ will undergo hydrolysis because it is a weak acid ($NH_4^+$ is the conjugate acid of the weak base, $NH_3$).

**Step 1:** Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown $x$, that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of $NH_4^+$. From the stoichiometry of the reaction, it follows that the increase in concentration for both $H_3O^+$ and $NH_3$ must be $x$. Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

\[
\text{NH}_4^+(aq) + H_2O(l) \rightleftharpoons \text{NH}_3(aq) + H_3O^+(aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>Change (M)</th>
<th>Equilibrium (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>$-x$</td>
<td>$(0.42 - x)$</td>
</tr>
<tr>
<td>0.00</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>$+x$</td>
</tr>
</tbody>
</table>

**Step 2:** You can calculate the $K_a$ value for $NH_4^+$ from the $K_b$ value of $NH_3$. The relationship is

\[
K_a \times K_b = K_w
\]
or

\[ K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \]

**Step 3:** Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant \((K_a)\), solve for \(x\).

\[ K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \]

\[ 5.6 \times 10^{-10} = \frac{x^2}{0.42 - x} \approx \frac{x^2}{0.42} \]

\[ x = [\text{H}_3\text{O}^+] = 1.5 \times 10^{-5} \text{ M} \]

\[ \text{pH} = -\log(1.5 \times 10^{-5}) = 4.82 \]

Since \(\text{NH}_4\text{Cl}\) is the salt of a weak base (aqueous ammonia) and a strong acid (HCl), we expect the solution to be slightly acidic, which is confirmed by the calculation.

16.75 The acid and base reactions are:

- **acid:** \(\text{HPO}_4^{2-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PO}_4^{3-}(aq)\)
- **base:** \(\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq)\)

\(K_a\) for \(\text{HPO}_4^{2-}\) is \(4.8 \times 10^{-13}\). Note that \(\text{HPO}_4^{2-}\) is the conjugate base of \(\text{H}_2\text{PO}_4^-\), so \(K_b\) is \(1.6 \times 10^{-7}\). Comparing the two \(K\)'s, we conclude that the monohydrogen phosphate ion is a much stronger proton acceptor (base) than a proton donor (acid). The solution will be basic.

16.76 \(\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}\) \[K_a = 4.8 \times 10^{-11}\]

\(\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-\) \[K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}\]

\(\text{HCO}_3^-\) has a greater tendency to hydrolyze than to ionize \((K_b > K_a)\). The solution will be basic \((\text{pH} > 7)\).

16.77 A Lewis base is a substance that can donate a pair of electrons, and a Lewis acid is a substance that can accept a pair of electrons. The Lewis concept is much more general than other definitions because it includes as acid-base reactions many reactions that do not involve Brønsted acids.

16.78 Lewis acids have a vacant orbital that can accept electrons – the \(1s\) in \(\text{H}^+\), and an unhybridized, vacant \(2p_\sigma\) in \(\text{BF}_3\). A Lewis base has a lone pair of electrons that can be donated to form a coordinate covalent bond. Both \(\text{OH}^-\) and \(\text{NH}_3\) have a lone pair that can be donated to a Lewis acid.

16.79 (a) Lewis acid; see the reaction with water shown in Section 16.11 of the text.

(b) Lewis base; water combines with \(\text{H}^+\) to form \(\text{H}_3\text{O}^+\).

(c) Lewis base.
(d) Lewis acid; \( \text{SO}_2 \) reacts with water to form \( \text{H}_2\text{SO}_3 \). Compare to \( \text{CO}_2 \) above. Actually, \( \text{SO}_2 \) can also act as a Lewis base under some circumstances.

(e) Lewis base; see the reaction with \( \text{H}^+ \) to form ammonium ion.

(f) Lewis base; see the reaction with \( \text{H}^+ \) to form water.

(g) Lewis acid; does \( \text{H}^+ \) have any electron pairs to donate?

(h) Lewis acid; compare to the example of \( \text{NH}_3 \) reacting with \( \text{BF}_3 \).

16.80 \( \text{AlCl}_3 \) is a Lewis acid with an incomplete octet of electrons and \( \text{Cl}^- \) is the Lewis base donating a pair of electrons.

\[
\begin{array}{c}
\text{Cl} \\
\text{Al} \\
\text{Cl} \\
\end{array}
+ \text{Cl}^- \rightarrow \left[ \begin{array}{c}
\text{Cl} \\
\text{Al} \\
\text{Cl} \\
\end{array} \right]^-
\]

16.81 (a) Both molecules have the same acceptor atom (boron) and both have exactly the same structure (trigonal planar). Fluorine is more electronegative than chlorine so we would predict based on electronegativity arguments that boron trifluoride would have a greater affinity for unshared electron pairs than boron trichloride.

(b) Since it has the larger positive charge, iron(III) should be a stronger Lewis acid than iron(II).

16.82 By definition Bronsted acids are proton donors, therefore such compounds must contain at least one hydrogen atom. In Problem 16.79, Lewis acids that do not contain hydrogen, and therefore are not Brønsted acids, are \( \text{CO}_2, \text{SO}_2, \) and \( \text{BCl}_3 \). Can you name others?

16.83 (a) acidic, (b) basic, (c) basic, (d) acidic, (e) neutral, (f) neutral, (g) amphoteric, (h) acidic, (i) amphoteric, (j) basic.

16.84 We first find the number of moles of \( \text{CO}_2 \) produced in the reaction:

\[
0.350 \frac{\text{g NaHCO}_3}{84.01 \frac{\text{g NaHCO}_3}{\text{mol}}} \times \frac{1 \text{ mol NaHCO}_3}{1 \text{ mol CO}_2} = 4.17 \times 10^{-3} \text{ mol CO}_2
\]

\[
V_{\text{CO}_2} = \frac{n_{\text{CO}_2} RT}{P} = \frac{(4.17 \times 10^{-3} \text{ mol})(0.0821 \text{ L atm} / \text{ mol} \cdot \text{K})(37.0 + 273)\text{K}}{(1.00 \text{ atm})} = 0.106 \text{ L}
\]

16.85 Choice (c) because 0.70 \( M \) KOH has a higher pH than 0.60 \( M \) NaOH. Adding an equal volume of 0.60 \( M \) NaOH lowers the \([\text{OH}^-]\) to 0.65 \( M \), hence lowering the pH.

16.86 If we assume that the unknown monoprotic acid is a strong acid that is 100% ionized, then the \([\text{H}^+]\) concentration will be 0.0642 \( M \).

\[
\text{pH} = -\log(0.0642) = 1.19
\]

Since the actual pH of the solution is higher, the acid must be a weak acid.
16.87 (a) \(\text{NH}_4^+\) and \(\text{NH}_3\) are a conjugate acid and base pair. \(\text{NH}_3\) and \(\text{NH}_2^-\) are a conjugate acid and base pair.  
(b) \(\text{H}^+\) corresponds to \(\text{NH}_4^+\); \(\text{OH}^-\) corresponds to \(\text{NH}_2^-\). For the neutral solution, \([\text{NH}_4^+] = [\text{NH}_2^-]\).

16.88 The reaction of a weak acid with a strong base is driven to completion by the formation of water. Irrespective of whether the strong base is reacting with a strong monoprotic acid or a weak monoprotic acid, the same number of moles of acid is required to react with a constant number of moles of base. Therefore the volume of base required to react with the same concentration of acid solutions (either both weak, both strong, or one strong and one weak) will be the same.

16.89 The balanced equation is: \(\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\)

\[
\text{mol of Mg} = 1.87 \text{ g/Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g/Mg}} = 0.0769 \text{ mol}
\]

From the balanced equation:

\[
\text{mol of HCl required for reaction} = 2 \times \text{mol Mg} = 2 \times 0.0769 \text{ mol} = 0.154 \text{ mol HCl}
\]

The concentration of HCl before reaction is:

\[
\text{pH} = -0.544, \text{ thus } [\text{H}^+] = 3.50 M
\]

\[
\text{mol HCl} = M \times \text{Vol (L)} = 3.50 M \times 0.0800 \text{ L} = 0.280 \text{ mol HCl}
\]

Moles of HCl left after reaction:

\[
\text{total mol HCl} - \text{mol HCl reacted} = 0.280 \text{ mol} - 0.154 \text{ mol} = 0.126 \text{ mol HCl}
\]

Molarity of HCl left after reaction:

\[
M = \text{mol/L} = 0.126 \text{ mol}/0.080 \text{ L} = 1.58 M
\]

\[
\text{pH} = -0.20
\]

16.90 High oxidation state leads to covalent compounds and low oxidation state leads to ionic compounds. Therefore, \(\text{CrO}\) is ionic and basic and \(\text{CrO}_3\) is covalent and acidic.

16.91 (a) \(\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2\)

\(\text{H}_2\) and \(\text{H}^-\) are a conjugate acid/base pair, and \(\text{H}_2\text{O}\) and \(\text{OH}^-\) are a conjugate acid/base pair.

(b) \(\text{H}^-\) is the reducing agent and \(\text{H}_2\text{O}\) is the oxidizing agent.

16.92 We can write two equilibria that add up to the equilibrium in the problem.

\[
\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

\[
K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}
\]

\[
\text{H}^+(aq) + \text{NO}_2^-(aq) \rightleftharpoons \text{HNO}_2(aq)
\]

\[
K_a = \frac{1}{K_a(\text{HNO}_2)} = \frac{1}{4.5 \times 10^{-4}} = 2.2 \times 10^3
\]

\[
\text{CH}_3\text{COOH}(aq) + \text{NO}_2^-(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{HNO}_2(aq)
\]

\[
K = \frac{[\text{CH}_3\text{COO}^-][\text{HNO}_2]}{[\text{CH}_3\text{COOH}][\text{NO}_2^-]} = K_a \times K_a'
\]
The equilibrium constant for this sum is the product of the equilibrium constants of the component reactions.

\[ K = K_a \times K'_a = (1.8 \times 10^{-5})(2.2 \times 10^3) = 4.0 \times 10^{-2} \]

16.93 In this specific case the \( K_a \) of ammonium ion is the same as the \( K_b \) of acetate ion. The two are of exactly (to two significant figures) equal strength. The solution will have \( \text{pH} 7.00 \).

What would the pH be if the concentration were 0.1 \( M \) in ammonium acetate? 0.4 \( M \)?

16.94 Let Nov represent the novocaine molecule which is a weak base in water.

\[ \text{Nov} + \text{H}_2\text{O} \leftrightharpoons \text{NovH}^+ + \text{OH}^- \]

\[ K_b = \frac{[\text{NovH}^+][\text{OH}^-]}{[\text{Nov}]} \]

Calculate the \([\text{OH}^-]\) from the pH.

\[ \text{pH} = 7.40 \quad \text{and} \quad \text{pOH} = 6.60 \]

\[ [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-6.60} = 2.5 \times 10^{-7} \text{ M} \]

Substitute the \([\text{OH}^-]\) into the \( K_b \) expression.

\[ 8.91 \times 10^{-6} = \frac{[\text{NovH}^+](2.5 \times 10^{-7} \text{ M})}{[\text{Nov}]} \]

\[ \frac{[\text{NovH}^+]}{[\text{Nov}]} = 36 \]

This is the ratio of the concentration of the acid to that of its base. The ratio of the concentration of the base to that of its acid is:

\[ \frac{[\text{Nov}]}{[\text{NovH}^+]} = \frac{1}{36} = 0.028 \]

16.95 (a) We carry an additional significant figure throughout this calculation to minimize rounding errors.

Number of moles \( \text{NaOH} = M \times \text{vol} (\text{L}) = 0.0568 \times 0.0138 \text{ L} = 7.838 \times 10^{-4} \text{ mol} \)

If the acid were all dimer, then:

\[ \text{mol of dimer} = \frac{\text{mol} \text{ NaOH}}{2} = \frac{7.838 \times 10^{-4} \text{ mol}}{2} = 3.919 \times 10^{-4} \text{ mol} \]

If the acetic acid were all dimer, the pressure that would be exerted would be:

\[ P = \frac{nRT}{V} = \frac{(3.919 \times 10^{-4} \text{ mol})(0.0821 \text{ L atm/K mol})(324 \text{ K})}{0.360 \text{ L}} = 0.02896 \text{ atm} \]
However, the actual pressure is 0.0342 atm. If $\alpha$ mol of dimer dissociates to monomers, then $2\alpha$ monomer forms.

\[
(\text{CH}_3\text{COOH})_2 \rightleftharpoons 2\text{CH}_3\text{COOH}
\]

\[
1 - \alpha \quad 2\alpha
\]

The total moles of acetic acid is:

\[
\text{moles dimer + monomer} = (1 - \alpha) + 2\alpha = 1 + \alpha
\]

Using partial pressures:

\[
P_{\text{observed}} = P(1 + \alpha)
\]

\[
0.0342 \text{ atm} = (0.02896 \text{ atm})(1 + \alpha)
\]

\[
\alpha = 0.181
\]

(b) The equilibrium constant is:

\[
K_P = \frac{P_{\text{CH}_3\text{COOH}}^2}{P_{(\text{CH}_3\text{COOH})_2}(P_{\text{observed}})} = \left(\frac{(X_{\text{CH}_3\text{COOH}})(P_{\text{observed}})}{X_{(\text{CH}_3\text{COOH})_2}(P_{\text{observed}})}\right)^2
\]

\[
X_{\text{CH}_3\text{COOH}} = \frac{\text{mol CH}_3\text{COOH}}{\text{total mol}} = \frac{2\alpha}{1 + \alpha} = \frac{2(0.181)}{1 + 0.181} = 0.3065
\]

\[
X_{(\text{CH}_3\text{COOH})_2} = 1 - 0.3065 = 0.6935
\]

\[
K_P = \frac{[(0.3065)(0.0342)]^2}{(0.6935)(0.0342)} = 4.63 \times 10^{-3}
\]

16.96 $0.100 \text{ M Na}_2\text{CO}_3 \rightarrow 0.200 \text{ M Na}^+ + 0.100 \text{ M CO}_3^{2-}$

First stage:

\[
\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)
\]

Initial (M):

\[
\begin{array}{ccc}
0.100 & 0 & 0 \\
\end{array}
\]

Change (M):

\[
\begin{array}{ccc}
-x & +x & +x \\
\end{array}
\]

Equilibrium (M):

\[
\begin{array}{ccc}
0.100 - x & x & x \\
\end{array}
\]

\[
K_1 = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}
\]

\[
2.1 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}
\]

\[
x = 4.6 \times 10^{-3} \text{ M} = [\text{HCO}_3^-] = [\text{OH}^-]
\]

Second stage:

\[
\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)
\]

Initial (M):

\[
\begin{array}{ccc}
4.6 \times 10^{-3} & 0 & 4.6 \times 10^{-3} \\
\end{array}
\]

Change (M):

\[
\begin{array}{ccc}
-y & +y & +y \\
\end{array}
\]

Equilibrium (M):

\[
\begin{array}{ccc}
(4.6 \times 10^{-3}) - y & y & (4.6 \times 10^{-3}) + y \\
\end{array}
\]
\[ K_2 = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} \]

\[ 2.4 \times 10^{-8} = \frac{y(4.6 \times 10^{-3}) + y}{(4.6 \times 10^{-3}) - y} \approx \frac{(y)(4.6 \times 10^{-3})}{(4.6 \times 10^{-3})} \]

\[ y = 2.4 \times 10^{-8} \text{ M} \]

At equilibrium:

\[ [\text{Na}^+] = 0.200 \text{ M} \]

\[ [\text{HCO}_3^-] = (4.6 \times 10^{-3}) \text{ M} - (2.4 \times 10^{-8}) \text{ M} \approx 4.6 \times 10^{-3} \text{ M} \]

\[ [\text{H}_2\text{CO}_3] = 2.4 \times 10^{-8} \text{ M} \]

\[ [\text{OH}^-] = (4.6 \times 10^{-3}) \text{ M} + (2.4 \times 10^{-8}) \text{ M} \approx 4.6 \times 10^{-3} \text{ M} \]

\[ [\text{H}^+] = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-3}} = 2.2 \times 10^{-12} \text{ M} \]

16.97 \[ [\text{CO}_2] = kP = (2.28 \times 10^{-3} \text{ mol/L-atm}) (3.20 \text{ atm}) = 7.30 \times 10^{-3} \text{ M} \]

\[ \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq) \]

\[ (7.30 \times 10^{-3} - x) \text{ M} \]

\[ K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \]

\[ 4.2 \times 10^{-7} = \frac{x^2}{(7.30 \times 10^{-3}) - x} \approx \frac{x^2}{7.30 \times 10^{-3}} \]

\[ x = 5.5 \times 10^{-5} \text{ M} = [\text{H}^+] \]

\[ \text{pH} = 4.26 \]

16.98 When NaCN is treated with HCl, the following reaction occurs.

\[ \text{NaCN} + \text{HCl} \rightarrow \text{NaCl} + \text{HCN} \]

HCN is a very weak acid, and only partially ionizes in solution.

\[ \text{HCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CN}^-(aq) \]

The main species in solution is HCN which has a tendency to escape into the gas phase.

\[ \text{HCN}(aq) \rightleftharpoons \text{HCN(g)} \]

Since the HCN(g) that is produced is a highly poisonous compound, it would be dangerous to treat NaCN with acids without proper ventilation.
16.99 \[ \text{pH} = 2.53 = -\log[H^+] \]
\[ [H^+] = 2.95 \times 10^{-3} \text{M} \]

Since the concentration of $H^+$ at equilibrium is $2.95 \times 10^{-3}$ M, that means that $2.95 \times 10^{-3}$ M HCOOH ionized. Let's represent the initial concentration of HCOOH as $I$. The equation representing the ionization of formic acid is:

\[
\begin{align*}
\text{HCOOH(aq)} & \rightarrow \text{H}^+(aq) + \text{HCOO}^-(aq) \\
\text{Initial (M):} & \quad I \\
\text{Change (M):} & \quad -2.95 \times 10^{-3} \\
\text{Equilibrium (M):} & \quad I - (2.95 \times 10^{-3}) \\
\end{align*}
\]

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

\[ 1.7 \times 10^{-4} = \frac{(2.95 \times 10^{-3})^2}{I - (2.95 \times 10^{-3})} \]

\[ I = 0.054 \text{M} \]

There are 0.054 mole of formic acid in 1000 mL of solution. The mass of formic acid in 100 mL is:

\[ \frac{100 \text{ mL} \times 0.054 \text{ mol formic acid}}{1000 \text{ mL soln}} \times \frac{46.03 \text{ g formic acid}}{1 \text{ mol formic acid}} = 0.25 \text{ g formic acid} \]

16.100 The equilibrium is established:

\[
\begin{align*}
\text{CH}_3\text{COOH(aq)} & \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \\
\text{Initial (M):} & \quad 0.150 \\
\text{Change (M):} & \quad -x \quad +x \\
\text{Equilibrium (M):} & \quad (0.150 - x) \quad x \\
\end{align*}
\]

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \]

\[ 1.8 \times 10^{-5} = \frac{x(0.100 + x)}{0.150 - x} \approx \frac{0.100x}{0.150} \]

\[ x = 2.7 \times 10^{-5} \text{M} \]

$2.7 \times 10^{-5}$ M is the $[H^+]$ contributed by CH$_3$COOH. HCl is a strong acid that completely ionizes. It contributes a $[H^+]$ of 0.100 M to the solution.

\[ [H^+]_{\text{total}} = [0.100 + (2.7 \times 10^{-5})] \text{M} \approx 0.100 \text{ M} \]

\[ \text{pH} = 1.000 \]

The pH is totally determined by the HCl and is independent of the CH$_3$COOH.

16.101 (a) The pH of the solution of HA would be lower. (Why?)

(b) The electrical conductance of the HA solution would be greater. (Why?)
(c) The rate of hydrogen evolution from the HA solution would be greater. Presumably, the rate of the reaction between the metal and hydrogen ion would depend on the hydrogen ion concentration (i.e., this would be part of the rate law). The hydrogen ion concentration will be greater in the HA solution.

16.102 The important equation is the hydrolysis of NO$_2^-$:

$$\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{OH}^-$$

(a) Addition of HCl will result in the reaction of the H$^+$ from the HCl with the OH$^-$ that was present in the solution. The OH$^-$ will effectively be removed and the equilibrium will shift to the right to compensate (more hydrolysis).

(b) Addition of NaOH is effectively addition of more OH$^-$ which places stress on the right hand side of the equilibrium. The equilibrium will shift to the left (less hydrolysis) to compensate for the addition of OH$^-$.

(c) Addition of NaCl will have no effect.

(d) Recall that the percent ionization of a weak acid increases with dilution (see Figure 16.4 of the text). The same is true for weak bases. Thus dilution will cause more hydrolysis, shifting the equilibrium to the right.

16.103 In Chapter 12, we found that salts with their formal electrostatic intermolecular attractions had low vapor pressures and thus high boiling points. Ammonia and its derivatives (amines) are molecules with dipole-dipole attractions; as long as the nitrogen has one direct N–H bond, the molecule will have hydrogen bonding.

Even so, these molecules will have much higher vapor pressures than ionic species. Thus, if we could convert the neutral ammonia-type molecules into salts, their vapor pressures, and thus associated odors, would decrease. Lemon juice contains acids which can react with neutral ammonia-type (amine) molecules to form ammonium salts:

$$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$$

$$\text{RNH}_2 + \text{H}^+ \rightarrow \text{RNH}_3^+$$

16.104

<table>
<thead>
<tr>
<th>HCOOH  $\rightarrow$ H$^+$ + HCOO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M): 0.400 0 0</td>
</tr>
<tr>
<td>Change (M): $-x$ $+x$ $+x$</td>
</tr>
<tr>
<td>Equilibrium (M): 0.400 $-x$ $x$ $x$</td>
</tr>
</tbody>
</table>

Total concentration of particles in solution: 

$$(0.400 - x) + x + x = 0.400 + x$$

Assuming the molarity of the solution is equal to the molality, we can write:

$$\Delta T_f = K_{fm}$$

$$0.758 = (1.86)(0.400 + x)$$

$$0.408 = 0.400 + x$$

$$x = 0.00800 = [\text{H}^+] = [\text{HCOO}^-]$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(0.00800)(0.00800)}{0.400 - 0.00800} = 1.6 \times 10^{-4}$$
16.105 (a) \[ \text{NH}_2^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^- \]
\[ \text{N}_3^- + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 + 3\text{OH}^- \]

\( \text{NH}_2^- \) and \( \text{N}_3^- \) are Brønsted bases and water is a Brønsted acid.

(b) \( \text{N}_3^- \) is the stronger base since each ion produces 3 \( \text{OH}^- \) ions.

16.106 \[ \text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}^+(aq) + \text{HSO}_3^-(aq) \]

Recall that 0.12 ppm \( \text{SO}_2 \) would mean 0.12 parts \( \text{SO}_2 \) per 1 million \( (10^6) \) parts of air by volume. The number of particles of \( \text{SO}_2 \) per volume will be directly related to the pressure.

\[ P_{\text{SO}_2} = \frac{0.12 \text{ parts } \text{SO}_2}{10^6 \text{ parts air}} = 1.2 \times 10^{-7} \text{ atm} \]

We can now calculate the \([\text{H}^+]\) from the equilibrium constant expression.

\[ K = \frac{[\text{H}^+][\text{HSO}_3^-]}{P_{\text{SO}_2}} \]
\[ 1.3 \times 10^{-2} = \frac{x^2}{1.2 \times 10^{-7}} \]
\[ x^2 = (1.3 \times 10^{-2})(1.2 \times 10^{-7}) \]
\[ x = 3.9 \times 10^{-5} \text{ M} = [\text{H}^+] \]
\[ \text{pH} = -\log(3.9 \times 10^{-5}) = 4.40 \]

16.107 In inhaling the smelling salt, some of the powder dissolves in the basic solution. The ammonium ions react with the base as follows:

\[ \text{NH}_4^+(aq) + \text{OH}^-(aq) \rightarrow \text{NH}_3(aq) + \text{H}_2\text{O} \]

It is the pungent odor of ammonia that prevents a person from fainting.

16.108 The fact that fluorine attracts electrons in a molecule more strongly than hydrogen should cause \( \text{NF}_3 \) to be a poor electron pair donor and a poor base. \( \text{NH}_3 \) is the stronger base.

16.109 Because the P–H bond is weaker, there is a greater tendency for \( \text{PH}_4^+ \) to ionize. Therefore, \( \text{PH}_3 \) is a weaker base than \( \text{NH}_3 \).

16.110 From the given pH's, we can calculate the \([\text{H}^+]\) in each solution.

Solution (1): \[ [\text{H}^+] = 10^{-\text{pH}} = 10^{-4.12} = 7.6 \times 10^{-5} \text{ M} \]
Solution (2): \[ [\text{H}^+] = 10^{-5.76} = 1.7 \times 10^{-6} \text{ M} \]
Solution (3): \[ [\text{H}^+] = 10^{-5.34} = 4.6 \times 10^{-6} \text{ M} \]
We are adding solutions (1) and (2) to make solution (3). The volume of solution (2) is 0.528 L. We are going to add a given volume of solution (1) to solution (2). Let's call this volume \( x \). The moles of \( H^+ \) in solutions (1) and (2) will equal the moles of \( H^+ \) in solution (3).

\[
\text{mol } H^+ \text{ soln (1)} + \text{mol } H^+ \text{ soln (2)} = \text{mol } H^+ \text{ soln (3)}
\]

Recall that \( \text{mol} = M \times L \). We have:

\[
(7.6 \times 10^{-5} \text{ mol/L})(x \text{ L}) + (1.7 \times 10^{-6} \text{ mol/L})(0.528 \text{ L}) = (4.6 \times 10^{-6} \text{ mol/L})(0.528 + x) \text{L}
\]

\[
(7.6 \times 10^{-5})x + (9.0 \times 10^{-7}) = (2.4 \times 10^{-6}) + (4.6 \times 10^{-6})x
\]

\[
(7.1 \times 10^{-5})x = 1.5 \times 10^{-6}
\]

\[
x = 0.021 \text{ L} = 21 \text{ mL}
\]

16.111 The equations are:

\[
\text{Cl}_2(g) + \text{H}_2\text{O(l)} \rightarrow \text{HCl(aq)} + \text{HClO(aq)}
\]

\[
\text{HCl(aq)} + \text{AgNO}_3(aq) \rightarrow \text{AgCl(s)} + \text{HNO}_3(aq)
\]

In the presence of \( \text{OH}^- \) ions, the first equation is shifted to the right:

\[
\text{H}^+ \text{ (from HCl)} + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

Therefore, the concentration of \( \text{HClO} \) increases. (The ‘bleaching action’ is due to \( \text{ClO}^- \) ions.)

16.112 The solution for the first step is standard:

<table>
<thead>
<tr>
<th>( \text{H}_3\text{PO}_4(aq) )</th>
<th>( \text{H}^+(aq) )</th>
<th>( \text{H}_2\text{PO}_4^-(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M):</td>
<td>0.100</td>
<td>0.000</td>
</tr>
<tr>
<td>Change (M):</td>
<td>(-x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equil. (M):</td>
<td>((0.100 - x))</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}
\]

\[
7.5 \times 10^{-3} = \frac{x^2}{(0.100 - x)}
\]

In this case we probably cannot say that \((0.100 - x) \approx 0.100\) due to the magnitude of \( K_{a1} \). We obtain the quadratic equation:

\[
x^2 + (7.5 \times 10^{-3})x - (7.5 \times 10^{-4}) = 0
\]

The positive root is \( x = 0.0239 \text{ M} \). We have:

\[
[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 \text{ M}
\]

\[
[\text{H}_3\text{PO}_4] = (0.100 - 0.0239) \text{ M} = 0.076 \text{ M}
\]

For the second ionization:

<table>
<thead>
<tr>
<th>( \text{H}_2\text{PO}_4(aq) )</th>
<th>( \text{H}^+(aq) )</th>
<th>( \text{HPO}_4^{2-}(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M):</td>
<td>0.0239</td>
<td>0.0239</td>
</tr>
<tr>
<td>Change (M):</td>
<td>(-y)</td>
<td>(+y)</td>
</tr>
<tr>
<td>Equil (M):</td>
<td>((0.0239 - y))</td>
<td>((0.0239 + y))</td>
</tr>
</tbody>
</table>
\[ K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \]

\[ 6.2 \times 10^{-8} = \frac{(0.0239 + y)(y)}{(0.0239 - y)} \approx \frac{(0.0239)(y)}{(0.0239)} \]

\[ y = 6.2 \times 10^{-8} M. \]

Thus,

\[ [H^+] = [H_2PO_4^-] = 0.0239 M \]

\[ [HPO_4^{2-}] = y = 6.2 \times 10^{-8} M \]

We set up the problem for the third ionization in the same manner.

\[
\begin{array}{c|c|c}
\text{HPO}_4^{2-} & \text{H}^+(aq) + \text{PO}_4^{3-} & \text{aq} \\
\text{Initial (M):} & 6.2 \times 10^{-8} & 0.0239 & 0 \\
\text{Change (M):} & -z & +z & +z \\
\text{Equil. (M):} & (6.2 \times 10^{-8}) - z & 0.0239 + z & z \\
\end{array}
\]

\[ K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \]

\[ 4.8 \times 10^{-13} = \frac{(0.0239 + z)(z)}{(6.2 \times 10^{-8}) - z} \approx \frac{(0.0239)(z)}{(6.2 \times 10^{-8})} \]

\[ z = 1.2 \times 10^{-18} M \]

The equilibrium concentrations are:

\[ [H^+] = [H_2PO_4^-] = 0.0239 M \]

\[ [H_3PO_4] = 0.076 M \]

\[ [HPO_4^{2-}] = 6.2 \times 10^{-8} M \]

\[ [PO_4^{3-}] = 1.2 \times 10^{-18} M \]

16.113 \( pOH = 3.36 \)

\[ [OH^-] = 4.4 \times 10^{-4} M \]

\[
\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq) \\
(I - 4.4 \times 10^{-4}) M \quad 4.4 \times 10^{-4} M \quad 4.4 \times 10^{-4} M \\
\]

\[ K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \]

\[ 4.4 \times 10^{-4} = \frac{(4.4 \times 10^{-4})(4.4 \times 10^{-4})}{I - (4.4 \times 10^{-4})} \]

\[ 4.4 \times 10^{-4} x - 1.9 \times 10^{-7} = 1.9 \times 10^{-7} \]

\[ I = 8.6 \times 10^{-4} M \]
The molar mass of CH₃NH₂ is 31.06 g/mol.

The mass of CH₃NH₂ in 100.0 mL is:

\[ 100.0 \text{ mL} \times \frac{8.6 \times 10^{-4} \text{ mol CH₃NH₂}}{1000 \text{ mL}} \times \frac{31.06 \text{ g CH₃NH₂}}{1 \text{ mol CH₃NH₂}} = 2.7 \times 10^{-3} \text{ g CH₃NH₂} \]

16.114 (a) The greater the percent ionization at a given solution concentration, the stronger the acid and the larger the \( K_a \) value. The amount of ionization can easily be determined by the number of hydronium ions, \( \text{H}_3\text{O}^+ \), produced. The acids arranged in order of increasing \( K_a \) are: \( \text{HY} < \text{HZ} < \text{HX} \).

(b) The stronger the acid, the weaker its conjugate base. The conjugate bases arranged in order of increasing \( K_b \) are: \( \text{X}^- < \text{Z}^- < \text{Y}^- \).

(c) In each diagram, there were 8 acid molecules present before ionization. The percent ionization is calculated by taking the number of hydronium ions, \( \text{H}_3\text{O}^+ \), produced divided by the initial number of acid molecules present and then multiplying by 100 to convert to a percentage.

\[
\% \text{ ionization} = \frac{\text{number of } \text{H}_3\text{O}^+ \text{ ions produced}}{\text{initial number of acid molecules}} \times 100\%
\]

% ionization of \( \text{HX} = \frac{6}{8} \times 100\% = 75\% 

% ionization of \( \text{HY} = \frac{2}{8} \times 100\% = 25\% 

% ionization of \( \text{HZ} = \frac{4}{8} \times 100\% = 50\% 

(d) These salts contain the conjugate bases of the acids shown in the diagrams. As mentioned in part (b) of this problem, the stronger the acid, the weaker its conjugate base. \( \text{HX} \) is the strongest acid of the three and therefore its conjugate base, \( \text{X}^- \), is the weakest. With all three salts having equal concentration, the weakest base will produce a solution with the lowest pH. Therefore, the salt solution with the lowest pH is \( \text{NaX} \).

16.115 Set up a table showing initial and equilibrium concentrations.

<table>
<thead>
<tr>
<th>HNO₂(aq)</th>
<th>( \text{H}^+(aq) )</th>
<th>NO₂⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (M):</td>
<td>0.80</td>
<td>0.00</td>
</tr>
<tr>
<td>Change (M):</td>
<td>(-x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium (M):</td>
<td>(0.80 – x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

Using the value of \( K_a \) from Table 16.3 of the text:

\[
K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}
\]

\[
4.5 \times 10^{-4} = \frac{x^2}{(0.80 - x)}
\]
We assume that \( x \) is small so \((0.80 - x) \approx 0.80\)

\[
4.5 \times 10^{-4} = \frac{x^2}{0.80}
\]

\( x = 0.019 \ M = [H^+] \)

\[\text{pH} = -\log(0.019) = 1.72\]

\[\text{Percent ionization} = \frac{0.019 \ M}{0.80 \ M} \times 100\% = 2.4\%\]

16.116 First, determine the molarity of each of the acids.

\[
M (HX) = \frac{16.9 \text{ g HX}}{1 \text{ L soln}} \times \frac{1 \text{ mol HX}}{180 \text{ g HX}} = 0.0939 \ M
\]

\[
M (HY) = \frac{9.05 \text{ g HY}}{1 \text{ L soln}} \times \frac{1 \text{ mol HY}}{78.0 \text{ g HY}} = 0.116 \ M
\]

Because both of these solutions have the same pH, they have the same concentration of \( \text{H}_3\text{O}^+ \) in solution. The acid with the lower concentration (\( HX \)) has the greater percent ionization and is therefore the stronger acid.

16.117 To calculate the \( K_a \) value of the acid, the molarity of the solution must be determined. The temperature, pressure, and density given will allow the calculation of the molar mass of the acid. Once the molar mass is known, the concentration of the acid can be determined. Knowing the concentration and the pH of the solution, the \( K_a \) value can then be calculated.

First, we calculate the moles of HA using the ideal gas equation, and then we calculate the molar mass of HA.

\[
n = \frac{PV}{RT} = \frac{(0.982 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L atm/mol K})(273 + 28) \text{K}} = 0.0397 \text{ mol}
\]

\[
\text{molar mass} = \frac{\text{g of substance}}{\text{mol of substance}} = \frac{1.16 \text{ g}}{0.0397 \text{ mol}} = 29.2 \text{ g/mol}
\]

The molarity of the acid solution is:

\[
M = \frac{\text{mol}}{\text{L}} = \frac{2.03 \text{ g} \times \frac{1 \text{ mol HA}}{29.2 \text{ g}}}{1.00 \text{ L}} = 0.0695 \ M
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>( \dot{c} )</th>
<th>( \text{H}^+ )</th>
<th>( \text{A}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>0.0695</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Change(M)</th>
<th>( -x )</th>
<th>( +x )</th>
<th>( +x )</th>
</tr>
</thead>
</table>

| Equil. (M) | \( 0.0695 - x \) | \( x \) | \( x \) |

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.0695 - x}
\]
The concentration of $H^+$, which equals $x$, can be determined from the pH of the solution.

$[H^+] = x = 10^{-pH} = 10^{-5.22} = 6.03 \times 10^{-6}$

$K_a = \frac{x^2}{0.0695 - x} = \frac{(6.03 \times 10^{-6})^2}{0.0695 - (6.03 \times 10^{-6})}$

$K_a = 5.2 \times 10^{-10}$

16.118 (a) The overall equation is

$$Fe_2O_3(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2O(l)$$

and the net ionic equation is

$$Fe_2O_3(s) + 6H^+(aq) \rightarrow 2Fe^{3+}(aq) + 3H_2O(l)$$

Since HCl donates the $H^+$ ion, it is the Brønsted acid. Each $Fe_2O_3$ unit accepts six $H^+$ ions; therefore, it is the Brønsted base.

(b) The first stage is

$$CaCO_3(s) + HCl(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) + Cl^-(aq)$$

and the second stage is

$$HCl(aq) + HCO_3^-(aq) \rightarrow CO_2(g) + Cl^-(aq) + H_2O(l)$$

The overall equation is

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The $CaCl_2$ formed is soluble in water.

(c) We need to find the concentration of the HCl solution in order to determine its pH. Let's assume a volume of $1.000 \text{ L} = 1000 \text{ mL}$. The mass of 1000 mL of solution is:

$$1000 \text{ mL} \times \frac{1.073 \text{ g}}{1 \text{ mL}} = 1073 \text{ g}$$

The number of moles of HCl in a 15 percent solution is:

$$\frac{15\% \text{ HCl}}{100\% \text{ soln}} \times 1073 \text{ g soln} = (1.6 \times 10^2 \text{ g} \text{HCl}) \times \frac{1 \text{ mol HCl}}{36.46 \text{ g} \text{HCl}} = 4.4 \text{ mol HCl}$$

Thus, there are 4.4 moles of HCl in one liter of solution, and the concentration is 4.4 $M$. The pH of the solution is

$$pH = -\log(4.4) = -0.64$$

This is a highly acidic solution (note that the pH is negative), which is needed to dissolve large quantities of rocks in the oil recovery process.
16.119 Given the equation: \( \text{HbH}^+ + \text{O}_2 \rightarrow \text{HbO}_2 + \text{H}^+ \)

(a) From the equilibrium equation, high oxygen concentration puts stress on the left side of the equilibrium and thus shifts the concentrations to the right to compensate. \( \text{HbO}_2 \) is favored.

(b) High acid \( \text{H}^+ \) concentration places stress on the right side of the equation forcing concentrations on the left side to increase, thus releasing oxygen and increasing the concentration of \( \text{HbH}^+ \).

(c) Removal of \( \text{CO}_2 \) decreases \( \text{H}^+ \) (in the form of carbonic acid), thus shifting the reaction to the right. More \( \text{HbO}_2 \) will form. Breathing into a paper bag increases the concentration of \( \text{CO}_2 \) (re-breathing the exhaled \( \text{CO}_2 \)), thus causing more \( \text{O}_2 \) to be released as explained above.

16.120 The balanced equations for the two reactions are:

\[
\text{MCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{MCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O(l)}
\]

\[
\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}
\]

First, let’s find the number of moles of excess acid from the reaction with \( \text{NaOH} \).

\[
0.03280 \text{L} \times \frac{0.588 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 0.0193 \text{ mol HCl}
\]

The original number of moles of acid was:

\[
0.500 \text{L} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L soln}} = 0.0500 \text{ mol HCl}
\]

The amount of hydrochloric acid that reacted with the metal carbonate is:

\[
(0.0500 \text{ mol HCl}) - (0.0193 \text{ mol HCl}) = 0.0307 \text{ mol HCl}
\]

The mole ratio from the balanced equation is 1 mole \( \text{MCO}_3 \) : 2 mole \( \text{HCl} \). The moles of \( \text{MCO}_3 \) that reacted are:

\[
0.0307 \text{ mol HCl} \times \frac{1 \text{ mol MCO}_3}{2 \text{ mol HCl}} = 0.01535 \text{ mol MCO}_3
\]

We can now determine the molar mass of \( \text{MCO}_3 \), which will allow us to identify the metal.

\[
\text{molar mass MCO}_3 = \frac{1.294 \text{ g MCO}_3}{0.01535 \text{ mol MCO}_3} = 84.3 \text{ g/mol}
\]

We subtract off the mass of \( \text{CO}_3^{2-} \) to identify the metal.

\[
\text{molar mass M} = 84.3 \text{ g/mol} - 60.01 \text{ g/mol} = 24.3 \text{ g/mol}
\]

The metal is \textit{magnesium}.

16.121 We start with the equation for the hydrolysis of a weak acid.

\[
\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-
\]
At equilibrium, \([\text{H}_3\text{O}^+] = [\text{A}^-]\).

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]}
\]

Because this is a weak acid, the concentration of HA at equilibrium is approximately equal to its initial concentration: \([\text{HA}] \approx [\text{HA}]_0\). Substituting into the above equation gives,

\[
K_a \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]_0}
\]

\[
[\text{H}_3\text{O}^+] = \sqrt{K_a[\text{HA}]_0}
\]

By definition,

\[
\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_0} \times 100\% = \sqrt{\frac{K_a[\text{HA}]_0}{[\text{HA}]_0}} = \sqrt{\frac{K_a}{[\text{HA}]_0}}
\]

Looking at this equation for \% ionization, when \([\text{HA}]_0\) is decreased by a factor of 10 to \(\frac{[\text{HA}]_0}{10}\), \% ionization increases by \(\sqrt{10}\). This result is in accord with LeChâtelier’s principle, which predicts that ionization should increase with dilution.

16.122 Because HF is a much stronger acid than HCN, we can assume that the pH is largely determined by the ionization of HF.

\[
\begin{array}{c|c|c|c}
\text{Initial (M)}: & 1.00 & 0 & 0 \\
\text{Change (M)}: & -x & +x & +x \\
\text{Equilibrium (M)}: & 1.00 - x & x & x \\
\end{array}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}
\]

\[
7.1 \times 10^{-4} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}
\]

\[
x = 0.027 \text{ M} = [\text{H}_3\text{O}^+] \\
\text{pH} = 1.57
\]

HCN is a very weak acid, so at equilibrium, \([\text{HCN}] \approx 1.00 \text{ M}\).

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

\[
4.9 \times 10^{-10} = \frac{(0.027)[\text{CN}^-]}{1.00}
\]

\[
[\text{CN}^-] = 1.8 \times 10^{-8} \text{ M}
\]
In a 1.00 M HCN solution, the concentration of [CN⁻] would be:

\[
\text{HCN(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>1.00</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>1.00 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

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

\[
4.9 \times 10^{-10} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}
\]

\[
x = 2.2 \times 10^{-5} \text{M} = [\text{CN}^-]
\]

[CN⁻] is greater in the 1.00 M HCN solution compared to the 1.00 M HCN/1.00 M HF solution. According to LeChâtelier’s principle, the high [H₃O⁺] (from HF) shifts the HCN equilibrium from right to left decreasing the ionization of HCN. The result is a smaller [CN⁻] in the presence of HF.

16.123 Both NaF and SnF₂ provide F⁻ ions in solution.

\[
\text{NaF} \rightarrow \text{Na}^+ + \text{F}^-
\]
\[
\text{SnF}_2 \rightarrow \text{Sn}^{2+} + 2\text{F}^-
\]

Because HF is a much stronger acid than H₂O, it follows that F⁻ is a much weaker base than OH⁻. The F⁻ ions replace OH⁻ ions during the remineralization process

\[
5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{F} \text{ (fluorapatite)}
\]

because OH⁻ has a much greater tendency to combine with H⁺

\[
\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}
\]

than F⁻ does.

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

Because F⁻ is a weaker base than OH⁻, fluorapatite is more resistant to attacks by acids compared to hydroxyapatite.

16.124 The van’t Hoff equation allows the calculation of an equilibrium constant at a different temperature if the value of the equilibrium constant at another temperature and ΔH° for the reaction are known.

\[
\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

First, we calculate ΔH° for the ionization of water using data in Appendix 2 of the text.

\[
\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)
\]

\[
\Delta H^\circ = [\Delta H^\circ_F(\text{H}^+)] + \Delta H^\circ_F(\text{OH}^-) - \Delta H^\circ_F(\text{H}_2\text{O})
\]

\[
\Delta H^F = (0 - 229.94 \text{ kJ/mol}) - (-285.8 \text{ kJ/mol})
\]

\[
\Delta H^F = 55.9 \text{ kJ/mol}
\]
We substitute \( \Delta H^\circ \) and the equilibrium constant at 25°C (298 K) into the van’t Hoff equation to solve for the equilibrium constant at 100°C (373 K).

\[
\ln \frac{1.0 \times 10^{-14}}{K_2} = \frac{55.9 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol·K}} \left( \frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} \right)
\]

\[
\frac{1.0 \times 10^{-14}}{K_2} = e^{-4.537}
\]

\[K_2 = 9.3 \times 10^{-13}\]

We substitute into the equilibrium constant expression for the ionization of water to solve for \([H^+]\) and then pH.

\[K_2 = [H^+][OH^-]\]

\[9.3 \times 10^{-13} = x^2\]

\[x = [H^+] = 9.6 \times 10^{-7} \text{ M}\]

\[\text{pH} = -\log(9.6 \times 10^{-7}) = 6.02\]

Note that the water is **not** acidic at 100°C because \([H^+] = [OH^-]\).