Chapter 13 – Acids and Bases

13.1 (a) strong base; (b) Bronsted-Lowry theory; (c) conjugate acid; (d) polyprotic acid; (e) acidic solution; (f) weak base; (g) amphoteric substance; (h) ion-product constant of water, $K_w$; (i) self-ionization

13.2 (a) strong acid; (b) Arrhenius model of acids and bases; (c) hydronium ion; (d) basic solution; (e) weak acid; (f) conjugate base; (g) acid ionization constant, $K_a$; (h) pH; (i) buffer

13.3 The significant figures of the log of a number are in the decimal portion of the number. The log of $7.4 \times 10^3$ is 3.87 because 3.87 has two decimal places. (a) $\log [10^{-7}] = -9$; (b) $\log [1 \times 10^{-11}] = -11.0$; (c) $\log [7.4 \times 10^3] = 3.87$; (d) $\log [10^5] = 5$; (e) $\log [1] = 0.0$

13.4 The significant figures of the log of a number are in the decimal portion of the number. The log of $1.7 \times 10^8$ is 8.23 because 8.23 has two decimal places. (a) $\log [10^4] = 4$; (b) $\log [1 \times 10^{-6}] = -6.0$; (c) $\log [1.7 \times 10^3] = 8.22$; (d) $\log [10^8] = 8$; (e) $\log [10] = 1.0$

13.5 The antilog button is often a second function of your log button. The antilog is calculated by raising 10 to the power of the logarithm (i.e. $10^x$). The significant figures are found in the decimal places. If a number has two decimal places, the answer should have two significant figures.

(a) $10^{1.2} = 15.8$ (this should be written as 20 since the answer should only have 1 significant figure). (b) $10^{-6.2} = 6.3 \times 10^{-7}$ (with significant figures); (c) $10^0 = 1$

13.6 The antilog button is often a second function of your log button. The antilog is calculated by raising 10 to the power of the logarithm (i.e. $10^x$). The significant figures are found in the decimal places. If a number has two decimal places, the answer should have two significant figures.

(a) $10^{12.7} = 5.0 \times 10^{12}$ (this should be written as $5 \times 10^{12}$ since the answer should only have 1 significant figure); (b) $10^{-9.4} = 4.0 \times 10^{-10}$ (with significant figures); (c) $10^1 = 10$

13.7 Acids taste sour (but you should never taste anything to see if it’s an acid!), are corrosive to many metals, turn blue litmus red, and neutralize bases.

13.8 Bases taste bitter (but you should never taste anything to see if it’s a base!), turn red litmus blue, and neutralize acids.

13.9 The list below includes some common “household” bases and their uses:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂</td>
<td>magnesium hydroxide</td>
<td>Antacid</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>aluminum hydroxide</td>
<td>Antacid</td>
</tr>
<tr>
<td>NH₃</td>
<td>ammonia</td>
<td>Cleaning solutions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Smelling Salts</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>calcium hydroxide</td>
<td>Concrete</td>
</tr>
</tbody>
</table>

13.10 The list below includes some common “household” acids and their uses:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
<td>Swimming pool acid</td>
</tr>
<tr>
<td>H₃C₆H₅O₄</td>
<td>acetylsalicylic acid</td>
<td>Aspirin</td>
</tr>
<tr>
<td>C₂H₄O₂H</td>
<td>acetic acid</td>
<td>Vinegar</td>
</tr>
<tr>
<td>H₂C₂H₄O₆</td>
<td>ascorbic acid</td>
<td>Vitamin C</td>
</tr>
</tbody>
</table>

13.11 An Arrhenius acid produces hydrogen ions ($H^+$) when it dissolves in water. An Arrhenius base produces hydroxide ion ($OH^-$) when it dissolves in water.
13.12 Electrolytes dissociate into ions when they dissolve in water. Arrhenius acids and bases are substances that produce hydronium and hydroxide ions, respectively, when they dissolve in water.

13.13 The Brønsted-Lowry theory of acids and bases focuses on the transfer of hydrogen ions from an acid to a base. While Arrhenius acids release hydrogen ions into a solution, Arrhenius bases are metal hydroxides (such as NaOH and KOH) that release OH\(^{-}\) ions into a solution. According to the Brønsted-Lowry theory, a base is any substance (including, but not limited to, OH\(^{-}\)) that can accept a hydrogen ion.

13.14 Hydrogen ions are very small and have a highly concentrated charge. It is unlikely that they could exist alone in solution. Instead, each hydrogen ion associates with one of the unshared electron pairs on a water molecule producing a hydronium ion H\(_3\)O\(^{+}\).

13.15 Acids donate hydrogen ions, and bases accept hydrogen ions. We can recognize an acid because, as a reactant, its formula will contain at least one H atom. As a product, its formula will be missing at least one H atom. Bases accept hydrogen ions, so their formulas gain at least one hydrogen ion during the reaction.
(a) HCN is an acid. After HCN donates its hydrogen ion, it becomes CN\(^{-}\).
(b) Sulfate, SO\(_4\)^{2-}, is a base. After it accepts a hydrogen ion, it becomes HSO\(_4\)^{-}.
(c) C\(_6\)H\(_5\)OH is an acid. After it donates a hydrogen ion, it becomes C\(_6\)H\(_5\)O\(^{-}\).

13.16 Acids donate hydrogen ions, and bases accept hydrogen ions. We can recognize an acid because, as a reactant, its formula will contain at least one H atom. As a product, its formula will be missing at least one H atom. Bases accept hydrogen ions, so their formulas gain at least one hydrogen ion during the reaction.
(a) CH\(_3\)CH\(_2\)NH\(_3\)^{+} is an acid. Its formula loses one hydrogen ion and becomes CH\(_3\)CH\(_2\)NH\(_2\).
(b) HCN is an acid. Its formula loses one hydrogen ion and becomes CN\(^{-}\).
(c) NaOH is a base. When it dissolves in water, NaOH releases hydroxide ion (OH\(^{-}\)) which gains hydrogen ions to become H\(_2\)O.

13.17 After an acid donates a hydrogen ion, its charge becomes more negative. For example, HNO\(_2\) becomes NO\(_2^{-}\). The species that remains after an acid donates a hydrogen ion (H\(^{+}\)) is the conjugate base of the acid.
(a) NO\(_2^{-}\);
(b) F\(^{-}\);
(c) H\(_2\)BO\(_3^{-}\).

13.18 After an acid donates a hydrogen ion, its charge becomes more negative. For example, HOCl becomes OCl\(^{-}\). The species that remains after an acid donates a hydrogen ion (H\(^{+}\)) is the conjugate base of the acid.
(a) OCl\(^{-}\);
(b) H\(_2\)PO\(_4^{-}\);
(c) CO\(_3^{2-}\).

13.19 When a base gains a hydrogen ion, its charge becomes more positive. For example, OH\(^{-}\) accepts H\(^{+}\) and becomes H\(_2\)O. The species that forms after the base gains a hydrogen ion (H\(^{+}\)) is the conjugate acid of the base.
(a) H\(_2\)O;
(b) C\(_6\)H\(_5\)NH\(_3\)^{+};
(c) H\(_2\)CO\(_3\).

13.20 When a base gains a hydrogen ion, its charge becomes more positive. For example, NH\(_3\) accepts H\(^{+}\) and becomes NH\(_4^{+}\). The species that forms after the base gains a hydrogen ion (H\(^{+}\)) is the conjugate acid of the base.
(a) NH\(_4^{+}\);
(b) HF;
(c) HCO\(_3^{-}\).

13.21 For convenience, when we write the chemical formulas of acids we indicate the acidic hydrogen atom first in the formula. Bases are substances with amine groups (–NH\(_2\) in chemical formulas), hydroxide ions, or selected anions in their formulas.
(a) HCl is an acid that donates a hydrogen ion to H\(_2\)O, forming H\(_3\)O\(^{+}\).

\[
\text{HCl}(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
\]

(b) HClO\(_4\) is an acid that donates a hydrogen ion to H\(_2\)O, forming H\(_3\)O\(^{+}\).

\[
\text{HClO}_4(l) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{ClO}_4^-(aq)
\]

(c) CH\(_3\)CO\(_2^{-}\) is a base that accepts a hydrogen ion from water to form CH\(_3\)COOH.

\[
\text{CH}_3\text{CO}_2^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HCH}_3\text{CO}_2(aq) + \text{OH}^-(aq)
\]
13.22 For convenience, when we write the chemical formulas of acids we indicate the acidic hydrogen atom first in the formula. Bases are substances with amine groups (−NH₂ in chemical formulas), hydroxide ions, or selected anions in their formulas.
(a) NaOH is a hydroxide-containing base. When it dissolves in water NaOH dissociates, releasing metal ions and hydroxide ions in solution.
\[
\text{NaOH}(s) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)
\]
(b) CN⁻ is a base that accepts a hydrogen ion from water to form HCN.
\[
\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HCN}(aq) + \text{OH}^-(aq)
\]
(c) HNO₃ is an acid that donates a hydrogen ion to water to form NO₃⁻ and H₂O⁺.
\[
\text{HNO}_3(l) + \text{H}_2\text{O}(l) \rightarrow \text{NO}_3^-(aq) + \text{H}_3\text{O}^+(aq)
\]

13.23 An amphoteric substance can both donate and accept hydrogen ions. Both water (a) and hydrogen sulfite (b) are amphoteric. Sulfate (c) cannot be amphoteric because it lacks a hydrogen ion to donate.

13.24 An amphoteric substance can both donate and accept hydrogen ions. Both (b) HBO₃²⁻ and (c) H₂PO₄⁻ are amphoteric. Ammonium ions, (a) NH₄⁺, are not amphoteric because they lack unshared electron pairs with which to accept an additional hydrogen ion.

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{H}
\end{array}
\]

13.25 Carbonic acid has two acidic hydrogen atoms. In polyatomic oxoanions (anions containing oxygen) acidic hydrogen atoms are always connected to oxygen atoms.

13.26 Phenol has only one acidic hydrogen atom (the hydrogen atom attached to the oxygen atom).

13.27 When strong acids dissolve in water, 100% of the dissolved molecules ionize. When weak acids dissolve in water, the percentage of molecules that ionize is much lower (typically, 5% or less). This means that when we dissolve 100 strong acid molecules in water, 100 H₂O⁺ ions form, leaving none of the unionized acid molecules. When we dissolve 100 weak acid molecules in water, only a few of them ionize and produce H₂O⁺ ions. As a result, most of the weak acid molecules remain unionized in solution. When strong bases dissolve in water, 100% of the dissolved molecules ionize to produce OH⁻ ions. In contrast, molecules of weak bases remain largely unionized.

13.28 For acids, this means that only a small fraction of the molecules react with water to form ions. For example, HCN is a weak acid. When we add HCN to water, the following equilibrium reaction takes place:
\[
\text{HCN}(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CN}^-(aq) + \text{H}_3\text{O}^+(aq)
\]
This equilibrium is very reactant-favored. Since the acid only partially ionizes, only a small percentage of the HCN molecules form ions.
We see an analogous behavior for weak bases:
\[
\text{NH}_3(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]
NH₃ is a weak base. The equilibrium above is also very reactant-favored. Thus, the base only partially ionizes; only a small percentage of the NH₃ molecules form ions.

13.29 Refer to Table 13.1 & 13.2 for lists of strong acids and bases. Consult Tables 13.3 and 13.4 for lists of commonly-encountered weak acids and weak bases. Practically, it is helpful to learn a short list of strong acids and bases, and then to consider any acids or bases that are not on the list as if they were weak (see
(d). Most commonly-encountered weak bases contain nitrogen, in the form of an amine (–NH₂), in their formulas or are conjugate bases of weak acids.

(a) strong acid (Table 13.1); \( H₂SO₄(\text{aq}) + H₂O(l) \rightarrow HSO₄⁻(\text{aq}) + H₃O⁺(aq) \)

(b) strong base (Table 13.2); \( \text{Ca(OH)}₂(\text{aq}) \rightarrow \text{Ca}^{²⁺}(\text{aq}) + 2\text{OH}⁻(\text{aq}) \)

(c) weak base (conjugate base of a weak acid); \( \text{Na}_₂\text{CO}_₃(\text{aq}) + H₂O(l) \rightleftharpoons \text{HCO}_₃⁻(\text{aq}) + 2\text{Na}⁺(\text{aq}) + \text{OH}⁻(aq) \)

(d) weak acid (not on the strong acid list); \( \text{H}_₃\text{C}_₆\text{H}_₅\text{O}_₇(\text{aq}) + H₂O(l) \rightleftharpoons \text{H}_₃\text{O}⁺(\text{aq}) + \text{H}_₂\text{C}_₆\text{H}_₅\text{O}_₇⁻(aq) \)

(e) weak base (amine); \( \text{C}_₆\text{H}_₅\text{NH}_₂ + H₂O(l) \rightleftharpoons \text{C}_₆\text{H}_₅\text{NH}_₃⁺(aq) + \text{OH}⁻(aq) \)

13.30 Refer to Table 13.1 & 13.2 for lists of strong acids and bases. Consult Tables 13.3 and 13.4 for lists of commonly-encountered weak acids and weak bases. Practically, it is helpful to learn a short list of strong acids and bases, and then to consider any acids or bases that are not on the list as if they were weak (see (d)). Most commonly-encountered weak bases contain nitrogen, in the form of an amine (–NH₂), in their formulas or are conjugate bases of weak acids.

(a) weak acid (not on the strong acid list); \( \text{HCN}(\text{aq}) + H₂O(l) \rightleftharpoons H₃O⁺(\text{aq}) + \text{CN}⁻(aq) \)

(b) weak base (conjugate base of weak acid); \( \text{NaCN}(\text{aq}) + H₂O(l) \rightleftharpoons \text{HCN}(\text{aq}) + \text{Na}⁺(\text{aq}) + \text{OH}⁻(aq) \)

(c) strong base (Table 13.2); \( \text{LiOH}(\text{aq}) \rightarrow \text{Li}⁺(aq) + \text{OH}⁻(aq) \)

(d) weak base (amine); \( \text{CH}_₃\text{NH}_₂ + H₂O(l) \rightleftharpoons \text{CH}_₃\text{NH}_₃⁺(aq) + \text{OH}⁻(aq) \)

(e) weak acid (not on the strong acid list); \( \text{H}_₂\text{C}_₂\text{O}_₄(\text{aq}) + H₂O(l) \rightleftharpoons H₃O⁺(aq) + \text{HC}_₂\text{O}_₄⁻(aq) \)

13.31 Image A represents \( \text{NH}_₃ \). \( \text{NH}_₃ \) is a weak base, so it only partially ionizes in water. Therefore, we see only a few hydroxide and ammonium ions in relation to the number of unionized \( \text{NH}_₃ \) molecules present. Image B represents \( \text{HF} \). \( \text{HF} \) is a weak acid, so it only partially ionizes in water. Therefore, we see only a few hydronium ions and fluoride ions in relation to the number of \( \text{HF} \) molecules in the image. Image C represents \( \text{HCl} \). \( \text{HCl} \) is a strong acid, so it ionizes completely in solution. Therefore, we see none of the original \( \text{HCl} \) molecules, but only hydronium ions and chloride ions.

13.32 (a) \( \text{Ba(OH)}₂ \) is a strong base, so it completely ionizes in the solution. The image should not include any \( \text{Ba(OH)}₂ \) formula units and should show a 1:2 ratio of \( \text{Ba}^{²⁺} \) and \( \text{OH}⁻ \).

(b) \( \text{NaOH} \) is a strong base, so it completely ionizes in the solution. The image should not include any \( \text{NaOH} \) formula units and should show a 1:1 ratio of \( \text{Na}⁺ \) and \( \text{OH}⁻ \).

(c) \( \text{HOCl} \) is a weak acid, so it only partially ionizes in solution. The image should show \( \text{HOCl} \) molecules mixed with \( H₂O \) molecules, and only a small number of hydronium ions and \( \text{OCl}⁻ \) ions (in a 1:1 ratio).

(a) \( \text{Ba(OH)}₂ \)  \hspace{1cm} (b) \( \text{NaOH} \)  \hspace{1cm} (c) \( \text{HOCl} \)

13.33 The conjugate base of a strong acid will not act as a base in solution (it is too weak to act as a base). Only the conjugate base of a weak acid will act as a weak base. \( \text{KBr} \) comes from \( \text{HBr} \) (strong acid) so it will not act as a base. \( \text{KF} \) is derived from the weak acid \( \text{HF} \) so will act as a base in solution.
13.34 The conjugate base of a strong acid will not act as a base in solution (it is too weak to act as a base). Only the conjugate base of a weak acid will act as a weak base. NaHCO$_3$ is related to the weak acid H$_2$CO$_3$. The bicarbonate ion, HCO$_3^-$, will act as a weak base. NaNO$_3$ is derived from HNO$_3$, a strong acid, so it will not behave as a weak base in solution (i.e. NO$_3^-$ is too weak to act as a base).

13.35 Acid A is a stronger acid than acid B. The stronger acid is the one that ionizes to the greater extent.

13.36 Acid D is a stronger acid than acid C. The magnitude of the acid ionization constant, $K_a$, is directly proportional to the strength of the acid.

13.37 Formic acid has a larger acid ionization constant, $K_a$, than acetic acid ($1.8 \times 10^{-4} > 1.8 \times 10^{-5}$). Therefore, a higher percentage of formic acid molecules than of acetic acid molecules ionize in water. Because the concentrations of the two acid solutions are the same and formic acid experiences a higher degree of ionization, the hydronium ion concentration will be higher in the formic acid solution than in the acetic acid solution.

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

13.38 HF has a larger acid ionization constant, $K_a$, than HNO$_2$ ($6.3 \times 10^{-4} > 5.6 \times 10^{-4}$). Therefore, HF ionizes to a greater degree in water than HNO$_2$ does.

13.39 A simple rule to remember is that the stronger acid produces the weaker conjugate base. The opposite is also true; a weaker acid makes a stronger conjugate base. Table 13.5 lists the acids HF and HCH$_3$CO$_2$ with their acid ionization constants. HCH$_3$CO$_2$ is the weaker acid, so its conjugate base will be stronger. A solution of NaCH$_3$CO$_2$ would be more basic and have a higher OH$^-$ concentration.

13.40 A simple rule to remember is that the stronger acid produces the weaker conjugate base. The opposite is also true; a weaker acid makes a stronger conjugate base. Table 13.5 lists the acids HOCl and HNO$_2$ with their acid ionization constants. HOCl is the weaker acid so its conjugate base will be stronger. This means that a solution of KOCl will be more basic (have a higher OH$^-$ concentration).

13.41 A strong acid solution contains acid molecules that fully ionize in water. Regardless of whether the solution is concentrated or dilute, the acid molecules all ionize. A concentrated acid solution contains many acid molecules in a given volume but the acid molecules are not necessarily ionized to any great extent.

13.42 Yes. Even though strong acids ionize completely, very dilute strong acid solutions contain only very small concentrations of hydronium ions. Even though weak acids only partially ionize, the hydronium ion concentration in concentrated weak acid solutions can be very high.

13.43 A polyprotic acid is an acid with more than one acidic hydrogen atom. Diprotic acids have two acidic hydrogen atoms; triprotic acids have three acidic hydrogen atoms. We often refer to acids such as HCl as monoprotic acids.

13.44 Polyprotic acids have more than one acidic hydrogen atom (Table 13.6). Carbonic acid, H$_2$CO$_3$; sulfuric acid, H$_2$SO$_4$; and oxalic acid, H$_2$C$_2$O$_4$ are all polyprotic acids.

13.45 Hydrosulfuric acid is a weak acid with two acidic hydrogen atoms. The equations that correspond to the two $K_a$s are:

$$\text{H}_2\text{S(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HS}^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$\text{HS}^-\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{S}^{2-}\text{(aq)} + \text{H}_3\text{O}^+(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

13.46 The acid ionization constant for H$_2$S ($8.9 \times 10^{-8}$) is much larger than $K_a$ for HS$^-$ ($1.0 \times 10^{-19}$), so H$_2$S ionizes to a greater extent than HS$^-$ in water.
13.47 We begin by writing the ionization equations for oxalic acid:

\[ \text{H}_2\text{C}_2\text{O}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HC}_2\text{O}_4^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = 5.6 \times 10^{-2} \]
\[ \text{HC}_2\text{O}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{O}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = 1.5 \times 10^{-4} \]

We can find all of the following substances in an oxalic acid solution: H$_2$C$_2$O$_4$, HC$_2$O$_4^-$, C$_2$O$_4^{2-}$, H$_3$O$^+$, and H$_2$O. Oxalate ions, C$_2$O$_4^{2-}$, are present in the lowest concentration. Oxalate ions form from hydrogen oxalate, HC$_2$O$_4^-$. Only a small amount of hydrogen oxalate is formed in the first reaction, so an even smaller amount of oxalate ion, C$_2$O$_4^{2-}$, is produced by the second reaction.

13.48 We begin by writing the ionization equations for citric acid. A triprotic acid has three ionizable hydrogen atoms:

\[ \text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{C}_6\text{H}_5\text{O}_7^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = 7.4 \times 10^{-4} \]
\[ \text{H}_2\text{C}_6\text{H}_5\text{O}_7^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HC}_6\text{H}_5\text{O}_7^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = 1.7 \times 10^{-5} \]
\[ \text{HC}_6\text{H}_5\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{O}_7^{3-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a3} = 4.0 \times 10^{-7} \]

We can find all of the following substances in a citric acid solution: H$_3$C$_6$H$_5$O$_7$, H$_2$C$_6$H$_5$O$_7^-$, HC$_6$H$_5$O$_7^{2-}$, C$_6$H$_5$O$_7^{3-}$, C$_6$H$_5$O$_7^{3-}$, H$_3$O$^+$, and H$_2$O. Citrate ions, C$_6$H$_5$O$_7^{3-}$, are present in the lowest concentration. The percent ionization of each reaction is very small, so the quantity of citrate ions produced in solution has to be very small.

13.49 Like other equilibrium constants, $K_w$ remains constant so long as the temperature does not change.

13.50 Yes. The self-ionization constant for water represents the equilibrium:

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

When we add H$_3$O$^+$ or OH$^-$ to water, the equilibrium shifts to the left, but the equilibrium constant does not change. For example, if we add H$_3$O$^+$ the equilibrium shifts to the left, decreasing the OH$^-$ concentration in the solution. On a quantitative level, the equilibrium constant expression for the self-ionization of water is written: $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$. If the concentration of H$_3$O$^+$ increases, the concentration of OH$^-$ must decrease, because $K_w$ is a constant.

13.51 In pure water, $[\text{OH}^-] = [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$.

13.52 On a qualitative level, we consider Le Chatelier’s principle and the self-ionization reaction of water:

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

When we add an acid to water, we are effectively adding H$_3$O$^+$. This addition causes the equilibrium to shift to the left, decreasing the OH$^-$ concentration in the solution. On a quantitative level, the equilibrium constant expression for the self-ionization of water is written: $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$. If the concentration of H$_3$O$^+$ increases, the concentration of OH$^-$ must decrease, because $K_w$ is a constant.

When we add a base to water, we are effectively adding OH$^-$. This addition also causes the equilibrium to shift to the left, decreasing the H$_3$O$^+$ concentration in the solution. On a quantitative level, the equilibrium constant expression for the self-ionization of water is written: $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$. If the concentration of OH$^-$ increases, the concentration of H$_3$O$^+$ must decrease, because $K_w$ is a constant.

13.53 Refer to 13.11. (a) The solution is basic because the hydronium ion concentration is lower than the hydroxide ion concentration. (b) The solution is acidic because the H$_3$O$^+$ concentration is greater than $1.0 \times 10^{-7} \text{ M}$. (c) The solution is basic because the OH$^-$ concentration is greater than $1.0 \times 10^{-7} \text{ M}$. 

13-6
13.54 Refer to 13.11. (a) The solution is acidic because the OH\(^-\) concentration is lower than \(1.0 \times 10^{-7}\) M. (b) The solution is basic because the H\(_3\)O\(^+\) concentration is lower than \(1.0 \times 10^{-7}\) M. (c) The solution is acidic because the hydronium ion concentration is greater than the hydroxide ion concentration.

13.55 To calculate [H\(_3\)O\(^+\)] from [OH\(^-\)], we use the ion-product constant for water \(K_w = [H_3O^+][OH^-]\) where \(K_w = 1.0 \times 10^{-14}\).

\[
[H_3O^+] = \frac{K_w}{[OH^-]}
\]

(a) \[
[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} M = 1.0 \times 10^{-7} M
\]

Because [H\(_3\)O\(^+\)] < \(1.0 \times 10^{-7}\) M, the solution is basic.

(b) \[
[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} M = 1.0 \times 10^{-11} M
\]

Because [H\(_3\)O\(^+\)] > \(1.0 \times 10^{-7}\) M, the solution is acidic.

(c) \[
[H_3O^+] = \frac{1.0 \times 10^{-14}}{3.2 \times 10^{-4}} M = 3.1 \times 10^{-7} M
\]

Because [H\(_3\)O\(^+\)] > \(1.0 \times 10^{-7}\) M, the solution is acidic (but only very slightly acidic).

13.56 To calculate [OH\(^-\)] from [H\(_3\)O\(^+\)], we use the ion-product constant for water \(K_w = [H_3O^+][OH^-]\) where \(K_w = 1.0 \times 10^{-14}\).

\[
[OH^-] = \frac{K_w}{[H_3O^+]}
\]

(a) \[
[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} M = 1.0 \times 10^{-11} M
\]

Because [OH\(^-\)] < \(1.0 \times 10^{-7}\) M, the solution is acidic.

(b) \[
[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} M = 1.0 \times 10^{-9} M
\]

Because [OH\(^-\)] < \(1.0 \times 10^{-7}\) M, the solution is acidic.

(c) \[
[OH^-] = \frac{1.0 \times 10^{-14}}{7.3 \times 10^{-10}} M = 1.4 \times 10^{-5} M
\]

Because [OH\(^-\)] > \(1.0 \times 10^{-7}\) M, the solution is basic.

13.57 For solutions of strong, monoprotic acids, the hydronium ion concentration is equal to the acid concentration. To calculate the hydronium ion concentration in a solution of a strong base, we use the ion-product constant of water.

(a) [H\(_3\)O\(^+\)] = 0.010 M

(b) [H\(_3\)O\(^+\)] = 0.020 M

(c) \[
[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.015 M} = 6.7 \times 10^{-13} M
\]

13.58 For solutions of strong bases with one OH\(^-\), the hydroxide ion concentration is equal to the base concentration. To calculate the hydroxide ion concentration in a solution of a strong acid, we use the ion-product constant of water.

13-7
(a) \([\text{OH}^-] = 0.0010 \, M\)
(b) \([\text{OH}^-] = 0.0050 \, M\)
(c) \([\text{OH}^-] = \frac{K_w}{[\text{H}_2\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.0010 \, M} = 1.0 \times 10^{-11} \, M\)

13.59 Olivia’s garden became more acidic. A decrease in pH represents an increase in acidity.

13.60 The water in Jake’s pool becomes more basic during hot weather. An increase in pH means that the water is more basic.

13.61 The pH scale is a logarithmic scale. This means that every 10-fold increase in hydrogen ion concentration is represented by a 1 pH-unit change (i.e. \(\log 10 = 1\)). If the hydronium ion concentration increases by a factor of 10, the pH drops one unit.

13.62 The lower the pH, the lower the hydronium ion concentration. A difference of three pH units represents a 1000-fold concentration difference. For example, if the pH of solution B is 3.00, the hydronium ion concentration in solution B is \(1.0 \times 10^{-3} \, M\). If solution A has a pH of 6.00, it has a hydronium ion concentration of \(1.0 \times 10^{-6} \, M\). This means that the hydronium ion concentration in solution B is 1000 times greater than in solution A.

13.63 A 1 M HCl solution has a pH of about 0.0. However to get a pH of \(-1.0\), you would have to have a 10 M solution. Similarly, to get a pH of 15 you would have to have a 10 M NaOH solution. Practically speaking, most solutions of acids and bases are lower in concentration than 1 M so the pH scale typically ranges between 0 and 14. However, the pH values can exceed this range.

13.64 Yes. A pH = 0.00 corresponds to a hydronium ion concentration of \(1.0 \, M\). \(([\text{H}_2\text{O}^+] = 10^{0.00} = 1.0 \, M\). In strong acid solutions with concentrations greater than \(1.0 \, M\), the pH is less than 0.00. A pH greater than 14.00 corresponds to a hydroxide ion concentration greater than \(1.0 \, M\).

13.65 No. A solution is acidic if its pH is less than 7.00, so long as the temperature is 25°C.

13.66 For acidic solutions, pH < 7.00, so the pH range for acidic solution is from 0.00 to 6.99. For basic solutions, pH > 7.00, so the pH range for basic solutions is from 7.01 to 14.00.

13.67 pH is defined as \(-\log [\text{H}_2\text{O}^+]\). A solution with pH less than 7.0 is acidic. A solution with pH greater than 7.0 is basic.
   (a) pH = \(-\log(1.0 \times 10^{-3}) = 3.00\), acidic
   (b) pH = \(-\log(1.0 \times 10^{-13}) = 13.00\), basic
   (c) pH = \(-\log(3.4 \times 10^{-10}) = 9.47\), basic

13.68 pH is defined as \(-\log [\text{H}_2\text{O}^+]\). A solution with pH less than 7.0 is acidic. A solution with pH greater than 7.0 is basic.
   (a) pH = \(-\log(1.0 \times 10^{-3}) = 9.00\), basic
   (b) pH = \(-\log(1.0 \times 10^{-14}) = 14.00\), basic
   (c) pH = \(-\log(7.2 \times 10^{-3}) = 2.14\), acidic

13.69 There are two ways to calculate pH from \([\text{OH}^-]\). Which problem solving map you choose to follow is really a matter of preference. We will use map 1.

Problem solving map 1:
\[
\text{pOH} = -\log[\text{OH}^-] \quad \text{pOH} = \text{pH} + \text{pOH} = 14 \quad \text{pH}
\]

Problem solving map 2:
\[ [\text{OH}^-] \cdot K_w = [\text{H}_2\text{O}^+] [\text{OH}^-] \Rightarrow [\text{H}_2\text{O}^+] = \frac{[\text{OH}^-]}{K_w} \]

\[ \text{pH} = -\log([\text{H}_2\text{O}^+]) \rightarrow \text{pH} \]

(a) \( \text{pH} = 10.00 \), basic
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(1.0 \times 10^{-4}) = 4.00 \]
\[ \text{pH} = 14.00 - 4.00 = 10.00 \]

(b) \( \text{pH} = 7.00 \), neutral
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(1.0 \times 10^{-7}) = 7.00 \]
\[ \text{pH} = 14.00 - 7.00 = 7.00 \]

(c) \( \text{pH} = 4.91 \), acidic
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(8.2 \times 10^{-10}) = 9.09 \]
\[ \text{pH} = 14.00 - 9.09 = 4.91 \]

13.70 There are two ways to calculate pH from \([\text{OH}^-]\). Which problem solving map you choose to follow is really a matter of preference. We will use map 1.

Problem solving map 1:

\[ [\text{OH}^-] \Rightarrow \text{pOH} = -\log([\text{OH}^-]) \Rightarrow \text{pOH} + \text{pH} = 14 \Rightarrow \text{pH} \]

Problem solving map 2:

\[ [\text{OH}^-] \Rightarrow K_w = [\text{H}_2\text{O}^+] [\text{OH}^-] \Rightarrow [\text{H}_2\text{O}^+] \Rightarrow \text{pH} = -\log([\text{H}_2\text{O}^+]) \Rightarrow \text{pH} \]

(a) \( \text{pH} = 10.81 \), basic
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(6.4 \times 10^{-4}) = 3.19 \]
\[ \text{pH} = 14.00 - 3.19 = 10.81 \]

(b) \( \text{pH} = 14.00 \), basic
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(1.0) = 0.00 \]
\[ \text{pH} = 14.00 - 0.00 = 14.00 \]

(c) \( \text{pH} = 4.43 \), acidic
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(2.7 \times 10^{-10}) = 9.57 \]
\[ \text{pH} = 14.00 - 9.57 = 4.43 \]

13.71 (a) Because HNO\textsubscript{3} is a strong acid, we assume that the hydronium ion concentration is the same as the acid concentration.
\[ \text{pH} = -\log(0.010) = 2.00 \text{, acidic} \]

(b) HClO\textsubscript{4} is a strong acid.
\[ \text{pH} = -\log(0.020) = 1.70 \text{, acidic} \]

(c) NaOH is a strong base, so we assume that the hydroxide ion concentration is equal to the sodium hydroxide concentration.
\[ \text{pOH} = -\log([\text{OH}^-]) = -\log(0.015) = 1.82 \]
\[ \text{pH} = 14.00 - 1.82 = 12.18 \text{, basic} \]

13.72 (a) Because KOH is a strong base, we assume that the hydroxide ion concentration is equal to the potassium hydroxide concentration.
pOH = \(-\log[OH^-]\) = \(-\log(0.0010)\) = 3.00
pH = 14.00 \( - \) 3.00 = 11.00, basic

(b) NaOH is a strong base.

pOH = \(-\log[OH^-]\) = \(-\log(0.0050)\) = 2.30
pH = 14.00 \( - \) 2.30 = 11.70, basic

c) Because HCl is a strong acid, we assume that the hydronium ion concentration is the same as the acid concentration.
pH = \(-\log(0.0010)\) = 3.00, acidic

13.73 The underlined values are given in the problem. The equations that relate the variables are given below.

\[
\begin{align*}
pH &= -\log[H_3O^+] \\
pOH &= -\log[OH^-] \\
[H_3O^+] &= 10^{-pH} \\
[OH^-] &= 10^{-pOH} \\
K_w &= [H_3O^+][OH^-] = 1.0 \times 10^{-14}
\end{align*}
\]

<table>
<thead>
<tr>
<th>([H_3O^+])</th>
<th>([OH^-])</th>
<th>pH</th>
<th>pOH</th>
<th>Acidic or Basic?</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
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<td>5.00</td>
<td>9.00</td>
</tr>
<tr>
<td>b</td>
<td>(1.0 \times 10^{-10})</td>
<td>(1.0 \times 10^{-4})</td>
<td>10.00</td>
<td>4.00</td>
</tr>
<tr>
<td>c</td>
<td>(1.0 \times 10^{-6})</td>
<td>(1.0 \times 10^{-8})</td>
<td>6.00</td>
<td>8.00</td>
</tr>
<tr>
<td>d</td>
<td>(2.9 \times 10^{-9})</td>
<td>(3.5 \times 10^{-6})</td>
<td>8.54</td>
<td>5.46</td>
</tr>
<tr>
<td>e</td>
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<td>(9.0 \times 10^{-10})</td>
<td>4.95</td>
<td>9.05</td>
</tr>
</tbody>
</table>

13.74 The underlined values are given in the problem. The equations that relate the variables are given below.

\[
\begin{align*}
pH &= -\log[H_3O^+] \\
pOH &= -\log[OH^-] \\
[H_3O^+] &= 10^{-pH} \\
[OH^-] &= 10^{-pOH} \\
K_w &= [H_3O^+][OH^-] = 1.0 \times 10^{-14}
\end{align*}
\]

<table>
<thead>
<tr>
<th>([H_3O^+])</th>
<th>([OH^-])</th>
<th>pH</th>
<th>pOH</th>
<th>Acidic or Basic?</th>
</tr>
</thead>
<tbody>
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<td>(9.0 \times 10^{-10})</td>
<td>4.95</td>
<td>9.05</td>
</tr>
<tr>
<td>c</td>
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<td>(1.0 \times 10^{-6})</td>
<td>8.00</td>
<td>6.00</td>
</tr>
<tr>
<td>d</td>
<td>(1.0 \times 10^{-12})</td>
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<td>2.00</td>
</tr>
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<td>(2.2 \times 10^{-13})</td>
<td>1.35</td>
<td>12.65</td>
</tr>
</tbody>
</table>

13.75 pH = \(-\log(0.0050)\) = 2.30, pOH = 14 \( - \) 2.30 = 11.70. pH plus pOH equals 14.00 at 25°C.

13.76 pOH = \(-\log(0.050)\) = 1.30, pH = 14 \( - \) 1.30 = 12.70. pH plus pOH equals 14.00 at 25°C.

13.77 We determine the H_3O^+ concentration using the relationship: \([H_3O^+] = 10^{-pH}\).

(a) pH = 5.00, acidic (Table 13.7)
\[
[H_3O^+] = 10^{-5.00} = 1.0 \times 10^{-5} M
\]

(b) pH = 12.00, basic
\[
[H_3O^+] = 10^{-12.0} = 1.0 \times 10^{-12} M
\]

(c) pH = 5.90, acidic
\[
[H_3O^+] = 10^{-5.90} = 1.3 \times 10^{-6} M
\]
13.78 We determine pOH using the equation pH + pOH = 14.00 and then calculate the OH⁻ concentration using the relationship: \[\text{[OH}^-]\] = \(10^{-\text{pOH}}\).

(a) pH = 5.00, acidic (Table 13.7)
\[
\text{pOH} = 14.00 - 5.00 = 9.00 \\
\text{[OH}^-]\] = \(10^{-9.00} = 1.0 \times 10^{-9} \text{ M}\)

(b) pH = 11.00, basic
\[
\text{pOH} = 14.00 - 11.00 = 3.00 \\
\text{[OH}^-]\] = \(10^{-3.0} = 1.0 \times 10^{-3} \text{ M}\)

(c) pH = 12.80, basic
\[
\text{pOH} = 14.00 - 12.80 = 1.20 \\
\text{[OH}^-]\] = \(10^{-1.20} = 6.3 \times 10^{-2} \text{ M}\)

13.79 We determine the H₃O⁺ concentration using the relationship: \[\text{[H}_3\text{O}^+] = 10^{-\text{pH}}\].

(a) household ammonia, pH = 11.00, basic (Table 13.7)
\[
\text{[H}_3\text{O}^+] = 10^{-11.00} = 1.0 \times 10^{-11} \text{ M}\)

(b) blood, pH = 7.40, basic
\[
\text{[H}_3\text{O}^+] = 10^{-7.40} = 4.0 \times 10^{-8} \text{ M}\)

(c) lime juice, pH = 1.90, acidic
\[
\text{[H}_3\text{O}^+] = 10^{-1.90} = 1.3 \times 10^{-2} \text{ M}\)

13.80 We determine the H₃O⁺ concentration using the relationship: \[\text{[H}_3\text{O}^+] = 10^{-\text{pH}}\].

(a) orange juice, pH = 3.50, acidic (Table 13.7)
\[
\text{[H}_3\text{O}^+] = 10^{-3.50} = 3.2 \times 10^{-4} \text{ M}\)

(b) lye, pH = 14.00, basic
\[
\text{[H}_3\text{O}^+] = 10^{-14.00} = 1.0 \times 10^{-14} \text{ M}\)

(c) saliva, pH = 7.00, neutral
\[
\text{[H}_3\text{O}^+] = 10^{-7.00} = 1.0 \times 10^{-7} \text{ M}\)

13.81 We determine the OH⁻ concentration using the relationships: \[\text{[OH}^-]\] = \(10^{-\text{pOH}}\) and pH + pOH = 14.00.

(a) gastric juice, pH = 1.00, acidic (Table 13.7)
\[
\text{pOH} = 14.00 - \text{pH} = 14.00 - 1.00 = 13.00 \\
\text{[OH}^-]\] = \(10^{-13.00} = 1.0 \times 10^{-13} \text{ M}\)

(b) magnesium hydroxide, pH = 10.50, basic
\[
\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.50 = 3.50 \\
\text{[OH}^-]\] = \(10^{-3.50} = 3.2 \times 10^{-4} \text{ M}\)

(c) soft drink, pH = 3.60, acidic
\[
\text{pOH} = 14.00 - \text{pH} = 14.00 - 3.60 = 10.40 \\
\text{[OH}^-]\] = \(10^{-10.40} = 4.0 \times 10^{-11} \text{ M}\)

13.82 We determine the H₃O⁺ concentration using the relationships: \[\text{[H}_3\text{O}^+] = 10^{-\text{pH}}\] and pH + pOH = 14.00.

(a) lake water, pOH = 6.00
\[
\text{pH} = 14.00 - 6.00 = 8.00 \\
\text{[H}_3\text{O}^+] = 10^{-8.00} = 1.0 \times 10^{-8} \text{ M}\)

(b) coffee, pOH = 8.90
\[
\text{pH} = 14.00 - 8.90 = 5.10 \\
\text{[H}_3\text{O}^+] = 10^{-5.10} = 7.9 \times 10^{-6} \text{ M}\)

(c) borax, pOH = 4.50
\[
\text{pH} = 14.00 - 4.50 = 9.50 \\
\text{[H}_3\text{O}^+] = 10^{-9.50} = 3.2 \times 10^{-10} \text{ M}\)

13-11
13.83 Higher. The pH of a 0.010 M solution of a strong acid, which completely ionizes, is 2.0. Acetic acid is a weak acid, so the hydronium ion concentration in a 0.010 M acetic acid solution is less than 0.010 M, causing the pH of that solution to be higher than 2.0 (more basic).

13.84 Lower. The pH of a 0.010 M NaOH solution (NaOH is a strong base that completely ionizes) is 12.0. Ammonia is a weak base, so the hydroxide ion concentration in a 0.010 M ammonia solution is less than 0.010 M, causing the pH of that solution to be lower than 12.0 (more acidic).

13.85 Sodium hydroxide is a strong base. When NaOH dissolves in water, it dissociates into its ions:

\[ \text{NaOH}(s) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) \]

This means that the concentrations of NaOH and OH\^- are the same. If pH = 13.0, then pOH = 14.0 – 13.0 = 1.0. From the pOH we calculate the hydroxide ion concentration:

\[ [\text{OH}^-] = 10^{-1.0} = 0.1 \text{ M} \]

The NaOH concentration is 0.1 M.

13.86 Hydrochloric acid is a strong acid. When HCl dissolves in water, it completely ionizes:

\[ \text{HCl}(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \]

This means that the concentrations of HCl and H\(^3\)O\(^+\) are the same. From the pH, we calculate the hydronium ion concentration:

\[ [\text{H}_3\text{O}^+] = 10^{-2.0} = 0.01 \text{ M} \]

The HCl concentration is 0.01 M.

13.87 A pH meter typically gives measurements accurate to two decimal places (Figure 13.17). Other methods (pH paper or indicator solutions) generally give lower precision.

13.88 pH paper is inexpensive, convenient, and we can use it almost anywhere.

13.89 Acid-base indicators are typically colorful compounds that are also weak acids or bases. The colors of the acid and base forms of these compounds are different. Many natural food colors are acid-base indicators (i.e. colors from blueberry, purple cabbage, curry powder, etc.). Litmus is actually an extract from lichens.

13.90 Acid-base indicators are actually weak acids and bases themselves. We represent their acid forms by HIn, and the conjugate bases by In\(^-\).

13.91 The color range of an indicator indicates the pH range over which the indicator changes color. We can use the indicator hue to estimate the pH of a solution. The range over which an indicator changes color is usually about 1.5 pH units.

13.92 To have two color-change ranges, an indicator must be a diprotic acid. The loss of each hydrogen ion produces a color change in the indicator.

13.93 Thymolphthalein is a good choice. In a solution with pH less than about 9.2, thymolphthalein is colorless. Above that pH, thymolphthalein gradually shifts from colorless to blue.

13.94 Bromoresol green and methyl red would be good indicator choices for this task.

13.95 At pH 3.5, methyl orange should be red, with a small amount of yellow-orange.

13.96 At pH 8.8, thymol blue should be predominately blue, with a small amount of yellow (slightly green in appearance).
13.97 Thymol blue is red in solutions with pH less than 2.5, yellow in solutions with pH between about 2.5 and 8.0, and blue (or with a blue hue) in solutions with pH greater than 8.0. Thymol blue is blue in solutions with pH greater than 9.5.

13.98 Phenolphthalein is colorless in solutions with pH below 8.0, and pink (or shades of pink) in solutions with pH greater than 8.0.

13.99 A universal indicator is a mixture of several different indicators. The mixture is selected so the indicator undergoes many distinct color changes throughout a wide pH range. Many newer pH papers contain mixtures of several different indicators and we use a color chart to relate the indicator color to a solution pH.

13.100 Litmus paper only indicates whether a solution is acidic or basic, but gives no indication of how acidic or how basic the solution might be. Litmus turns red if the solution is acidic and blue if it is basic.

13.101 The color of indicators at different pH ranges is shown in Figure 13.18. Bromocresol green is yellow at low pH (i.e. pH = 1.0) and blue at high pH (i.e. greater than about 4.5). This means the solution would be yellow at the start of the titration and turn blue just past or very near the endpoint. If you are careful, you will observe the pale green color at the endpoint (a combination of yellow and blue).

13.102 The color of indicators at different pH ranges is shown in Figure 13.18. At high pH, methyl red is yellow and at low pH the color is red. The endpoint is the first persistence of red color in the yellow solution.

13.103 A buffered solution contains both a weak acid and its conjugate base (or a weak base and its conjugate acid). As a result, when small amounts of acid or base are added to the solution, the buffer can absorb (react with) the added hydronium ions or hydroxide ions with only a small change in pH. Weak acid solutions cannot absorb any added acid, and weak base solutions cannot absorb any added base.

13.104 Weak acids and their conjugate bases, or weak bases and their conjugate acids make good buffer combinations. Strong acids and bases (and their conjugate bases/ acids) do not make good buffers because they remain completely ionized and cannot absorb added acids or bases.

13.105 The buffer system in blood helps to maintain a pH between 7.35 and 7.45.

13.106 When we add a small amount of acid or base to a buffered solution, the pH change is much smaller than is the case when we add the same amount of acid or base to water. The buffer reacts with the added acid and base, greatly diminishing the changes to the hydronium ion or hydroxide ion concentrations these additions cause in unbuffered solutions.

13.107 Acetic acid (CH₃CO₂H) is a weak acid. To make a buffered solution, we should add any soluble ionic compound containing CH₃CO₂⁻, the conjugate base of CH₃CO₂H (e.g., NaCH₃CO₂).

13.108 Sulfate (SO₄²⁻) is the weak conjugate base of HSO₄⁻. Adding NaHSO₄ to the solution will produce a buffered solution.

13.109 (a) Na₃HPO₄ dissolves in water and produces sodium ions and hydrogen phosphate ions (HPO₄²⁻). Na₃PO₄ dissolves in water and produces Na⁺ and phosphate (PO₄³⁻) ions. Hydrogen phosphate, HPO₄²⁻, is the acid, and the conjugate base is phosphate, PO₄³⁻. The solution pH reflects the free hydronium ion concentration in the solution (“free” means “H₃O⁺ that is unreacted”).

\[
\text{HPO}_4^{2-} (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{PO}_4^{3-} (aq) + \text{H}_3\text{O}^+(aq)
\]

(b) When we add acid to this buffered solution, hydronium ions (H₃O⁺) are produced and the pH momentarily drops (more acidic). The added hydronium quickly reacts with the PO₄³⁻, shifting the equilibrium to the left to produce more HPO₄²⁻. Because most of the added hydronium ions are...
effectively consumed by the $\text{PO}_4^{3-}$, the pH change is not as large as would be the case if the buffer were not present.

13.110 (a) When we add sodium acetate to water, it dissociates to form sodium ions and acetate ions ($\text{CH}_3\text{CO}_2^-$), the conjugate base of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$. Acetic acid ionizes in water to produce acetate ions and hydronium ions. The solution pH reflects the free hydronium ion concentration in the solution ("free" means "H$_3$O" that is unreacted).

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

(b) When we add acid to the buffered solution, hydronium (H$_3$O$^+$) is produced, and the pH momentarily drops (the solution becomes more acidic). However, the added hydronium ions quickly react with the $\text{CH}_3\text{CO}_2^-$, shifting the equilibrium to the left to produce more $\text{CH}_3\text{CO}_2\text{H}$. Because most of the added hydronium ions are consumed by acetate ions, the pH change is not as large as would be the case if the buffer were not present.

13.111 The solutions described in (b) and (c) are buffered. To prepare a buffered solution we need both the weak acid and its conjugate base (or weak base and its conjugate acid) in approximately equal concentrations. The solution in (b) will contain $\text{HNO}_2$ (weak acid) and $\text{NO}_2^-$, the conjugate base of $\text{HNO}_2$ (potassium ions are spectators):

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

The solution in (c) contains $\text{CH}_3\text{NH}_2$ (weak base) and its conjugate acid, $\text{CH}_3\text{NH}_3^+$, (chloride ions are spectators) in the reaction:

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

In (a) NaCl is not the conjugate base of HOCl.

13.112 The solutions described in (a) and (c) are buffered. To prepare a buffered solution we need both the weak acid and its conjugate base in approximately equal concentrations. The solution in (a) will contain HF (weak acid) and F$^-$, the conjugate base of HF (sodium ions are spectators):

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

The solution in (c) contains $\text{HOCl}$ (weak acid) and its conjugate base $\text{OCl}^-$ (sodium ions are spectators):

$$\text{HOCl}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OCl}^-(aq) + \text{OH}^-(aq)$$

The solution in (b) contains HI and I$^-$, but I$^-$ is the conjugate base of a strong acid and cannot react with added H$_3$O$^+$ as it must for the buffer to be effective.

13.113 Carbon dioxide is a reactant in the reaction given:

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

As the concentration of carbon dioxide increases, the equilibrium of the reaction would shift to the right. This leads to the formation of carbonic acid, $\text{H}_2\text{CO}_3(aq)$. The ionization of carbonic acid would cause a decrease in the pH of the extracellular fluid.

13.114 Physical stress, such as that which accompanies a panic attack often leads to the production of excess CO$_2$. This CO$_2$ leads to a decrease in the blood pH through the production of carbonic acid. Because CO$_2(g)$ is a reactant in the reactions shown, as its concentration increases the equilibrium shifts to the right (Le Chatelier’s Principle) and hydrogen ion is produced.

$$\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}^+(aq)$$
13.115 There is an unshared electron pair on the nitrogen atom that gives ammonia, NH$_3$, its basic properties. The carbon atom in methane does not have an unshared electron pair, so it cannot accept a hydrogen ion (proton) in an acid-base reaction.

13.116 Yes. The stronger the acid, the more completely it ionizes. In addition, the hydronium ion concentration increases as the acid concentration in the solution increases. The hydronium ion concentration in solutions of strong acids (such as HNO$_3$ or HCl) varies only with acid concentration, because strong acids ionize completely in solution.

13.117 When NaF dissolves in water, sodium and fluoride ions are produced. The fluoride ions react with water to produce a weak acid, HF:

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

In general, the conjugate base of a weak acid (F$^-$ in this case) reacts to some extent with water, producing the weak acid and hydroxide ions. The resulting solution is slightly basic.

13.118 For each formula unit of Ba(OH)$_2$ that dissolves, one barium ion and two hydroxide ions form.

$$\text{Ba(OH)}_2(s) \rightarrow \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq)$$

In a 0.01 M Ba(OH)$_2$ solution, the Ba$^{2+}$ concentration is 0.01 M and the OH$^-$ concentration is 0.02 M. To calculate the solution pH, we can first calculate its pOH, and then use the relationship pH + pOH = 14.0 to determine pH.

\[
pOH = -\log[OH^-] = -\log(0.02 M) = 1.7
\]
\[
pH = 14.0 - pOH = 14.0 - 1.7 = 12.3
\]

13.119 No. At 25°C, a neutral solution (e.g. pure water) has pH = pOH = 7.00. If we add any sodium hydroxide to the solution, the hydroxide ion concentration will increase, giving the solution a pH greater than 7.00.

13.120 No. At 25°C, a neutral solution (e.g. pure water) has pH = pOH = 7.00. If we add any hydrochloric acid to the solution, the hydronium ion concentration will increase, giving the solution a pH less than 7.00.

13.121 Although both H$_2$SO$_4$ and HNO$_3$ are strong acids, the pH of the H$_2$SO$_4$ solution is lower. Both acids dissociate completely for the first ionization. However, H$_2$SO$_4$ is a polyprotic acid. The additional hydronium ion produced from the second ionization will make the pH of the sulfuric acid solution lower.

$$\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HSO}_4^-(aq) + \text{H}_3\text{O}^+(aq) \quad \text{completely ionized}$$

$$\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad \text{partially ionized}$$

13.122 (a) $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(aq)$

(b) $2\text{HCl}(aq) + 2\text{Na}(s) \rightarrow 2\text{NaCl}(aq) + \text{H}_2(g)$

13.123 (a) $\text{HOCl}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OCl}^-(aq) + \text{H}_3\text{O}^+(aq)$

(b) The added HCl reacts with the pool water, producing hydronium ions and chloride ions (HCl(aq) + H$_2$O(l) $\rightleftharpoons$ Cl$^-(aq) + H_3O^+(aq)$). The added H$_2$O$^+$ causes the HOCl/OCl$^-$ equilibrium to shift to the left, decreasing the impact of the added hydronium ion. The HOCl concentration increases and the
13.124 The acids, HCl, HNO₃, and HI are all strong acids. This means that they remain fully ionized in water. This means that Cl⁻, NO₃⁻, and I⁻ have no tendency to react with hydronium ions to form the unionized acids and thus do not act as bases.

13.125 Sulfuric acid is a strong polyprotic acid and is completely ionized. This can be illustrated in the series of reactions:

\[
\begin{align*}
H_2SO_4(aq) & \rightarrow H^+(aq) + HSO_4^-(aq) \\
HSO_4^-(aq) & \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)
\end{align*}
\]

A strong acid completely dissociates in the first reaction. In this case HSO₄⁻ is formed and all of the H₂SO₄ is consumed. As a result, H₂SO₄ is absent from the image. HSO₄⁻ is a much weaker acid than sulfuric acid, so very little of it dissociates.

13.126 Formic acid ionizes according to the reaction:

\[
HCO_2H(aq) \rightleftharpoons H^+(aq) + CO_2H^-(aq)
\]

The formate ion, CO₂H⁻, is the conjugate base of formic acid.

13.127 To prepare a buffer you must have both the acid and its conjugate base present in approximately equal concentrations. The simplest way to do this is to mix equal molar amounts of the acid and the salt of its conjugate base. In this example you might choose to mix formic acid and sodium formate (HCO₂H and NaCO₂H). You can also partially neutralize a solution of the acid with sodium hydroxide to get the same result. This works because the product of the reaction is sodium formate:

\[
HCO_2H(aq) + NaOH(aq) \rightarrow NaCO_2H(aq) + H_2O(l)
\]

13.128 The reactions are given as

\[
\begin{align*}
H_2C_6H_6O_6(aq) & \rightleftharpoons H^+(aq) + HC_6H_6O_6^-(aq) \\
HC_6H_6O_6^-(aq) & \rightleftharpoons H^+(aq) + C_6H_6O_6^{2-}(aq)
\end{align*}
\]

Because ascorbic acid is a weak acid, very little dissociates. The substance highest in concentration will be ascorbic acid. The next highest will be hydrogen ions. This happens because hydrogen ions are produced in the ionization of ascorbic acid and HC₆H₆O₆⁻ is a weak acid and partially ionizes to form more hydrogen ions (so its concentration goes down and the hydrogen ion concentration increases). Finally, the substance with lowest concentration is ascorbate ions (C₆H₆O₆²⁻). Its concentration is low because very few hydrogen ascorbate ions ionize (note the low ionization constant).

13.129 The acidic hydrogens are attached to oxygen atoms:
13.130 The pH of a solution can be calculated from the pOH of the solution. To calculate pOH, we must first calculate the concentration of hydroxide ion, OH\(^-\). Note that each mole of Ca(OH)\(_2\) supplies two moles of OH\(^-\), so the hydroxide ion concentration is given by:

\[
[\text{OH}^-] = \frac{2}{2} \times \frac{0.50 \text{ mol LiOH}}{0.50 \text{ mol LiOH} + 1.00 \text{ mol LiOH}} = 1.50 \text{ M OH}^-\]

Next, we convert this concentration to pOH:

\[
pOH = -\log [\text{OH}^-] = -\log (1.50) = -0.18
\]

To convert to pH, we use the relation:

\[
pH + pOH = 14.00
\]

Rearranging, we get:

\[
pH = 14.00 - pOH = 14.00 - (-0.18) = 14.00 + 0.18 = 14.18
\]

13.131 The following statements about acids are incorrect. Change each statement to make it correct.

(a) Some strong acids have H atoms bonded to electronegative oxygen atoms. (Binary acids generally do not contain oxygen atoms.)

(b) The conjugate base of a strong acid is itself a weak base.

(c) Strong acids may be very concentrated acids. (Acid strength is a measure of the extent to which the acid dissociates in water, not a measure of its concentration.)

(d) Strong acids produce solutions with a low pH. (Acidic solutions have a low pH, and basic solutions have a high pH.)

13.132 Let’s consider the volumes to be 1.0 L for each solution to simplify our calculations. The concentration of hydrogen ions in the first solution is:

\[
[H^+] = 10^{-pH} = 10^{-1.0} = 0.1 \text{ M}
\]

A volume of 1.0 L of this solution thus contains 0.10 mol H\(^+\).

For the second solution,

\[
[H^+] = 10^{-pH} = 10^{-6.0} = 1 \times 10^{-6} \text{ M}
\]

A volume of 1.0 L of this solution thus contains 1 \times 10^{-6} \text{ mol H}^+.

The new volume of solution is the sum of the two volumes that were mixed, or 2.0 L. The new concentration is:

\[
[H^+] = \frac{0.1 \text{ mol H}^+ + 1 \times 10^{-6} \text{ mol H}^+}{2.0 \text{ L}} = 0.05 \text{ mol/L} = 0.05 \text{ M}
\]
Finally, we calculate pH:

$$pH = -\log [H^+] = -\log (0.05) = 1.3$$

13.133 Under these conditions, $[H^+][OH^-] = 1.0 \times 10^{-13}$. Taking logarithms of both sides give us:

$$\log [H^+] + \log [OH^-] = \log (1.0 \times 10^{-13}) = -13.0$$

If we change the sign of each side of the equation, we get:

$$-\log [H^+] + -\log [OH^-] = -13.0$$

The left-hand terms are just the definitions of pH and pOH:

$$pH + pOH = 13.0$$

For pure water, $pH = pOH$, so we have:

$$pH + pH = 13.0 \text{ or } pH = 6.5$$

13.134 The weaker the acid, the stronger the conjugate base (see Table 13.5). The weakest acid is the one with the smallest value of $K_a$, which is HCN with $K_a = 6.2 \times 10^{-10}$.

13.135 Arranging the solutions in order of increasing hydroxide ion concentration is the same as arranging them in order of decreasing hydrogen ion concentration or increasing pH. We must first determine the pH of the solutions for which this information was not given.

- pH of 0.1 M HNO₃ = $-\log (0.1) = 1.0$
- pH of 0.5 M HCl = $-\log (0.5) = 0.3$
- Pure water has a pH of 7.0

We were given the pH of the other two solutions:

- a solution of HNO₂ with a pH of 4.0
- a buffer solution with a pOH of 11.0

We get the following order of increasing pH and increasing [OH⁻]:

$$0.5 \text{ M HCl} < 0.1 \text{ M HNO₃} < \text{ a solution of HNO₂ with a pH of 4.0} < \text{ water } < \text{ a buffer solution with a pOH of 11.0}$$

13.136 A buffer requires a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid. All of the mixtures listed have these combinations, except for (a) NaCl and CH₃CO₂H. A conjugate base of acetic acid would be a salt containing acetate ion, such as NaCH₃CO₂.

13.137 For a solution of sodium acetate to become a buffer, some acetic acid (its conjugate acid) must be present. This condition can be accomplished by adding acetic acid. It can also be accomplished by adding hydrochloric acid, which will react with acetate ion to form acetic acid.

13.138 When HCl(aq), a strong acid, is added to a solution containing nitrite ion (NO₂⁻) and nitrous acid (HNO₂), the HCl will react with nitrite ion to form nitrous acid. Thus, the concentration of nitrite ion will decrease, and the concentration of nitrous acid will increase.

13.139 Answer: D; as the acid HSO₄⁻ loses an H⁺ ion, it becomes its conjugate base, SO₄²⁻.

When the reaction runs in reverse, H₂CO₃(aq) is the acid because it transfers an H⁺ to SO₄²⁻.

13.140 Answer: B; the conjugate base (HPO₄²⁻) differs from its acid (H₂PO₄⁻) by an H⁺.

A. The conjugate acid of H₂PO₄⁻ is H₃PO₄.

13.141 Answer: A; substances that ionize in water to form H₂O⁺ are acids because they transfer H⁺ to the H₂O molecules. When only a fraction of the acid ionizes, it’s a weak acid. (A strong acid would ionize completely so the concentration of H₂O⁺ ions is the same as that of the unionized acid.)

B. A 0.50 M monoprotic strong acid would ionize completely to form 0.50 M its conjugate base and 0.50 M H₂O⁺.

C. A 0.50 M weak base would ionize in water to a small extent, generating concentrations of its conjugate acid and OH⁻ that are much smaller than 0.50 M.
D. A strong base that is a metal hydroxide would dissociate completely in water forming aqueous metal cations and OH\(^{-}\) ions.

E. A neutral salt would dissociate completely in water forming cations and anions, but would not generate OH\(^{-}\) or H\(_3\)O\(^{+}\) ions.

13.142 Answer: B; the reaction that forms an equilibrium is CH\(_3\)NH\(_2\)(aq) + H\(_2\)O(l) ⇌ CH\(_3\)NH\(_3\)(aq) + OH\(^{-}\)(aq).

Because an equilibrium is formed, all reactants and products are present in the solution at equilibrium.

Water is highest in concentration because it is the solvent. The weak base is second highest because only a small fraction of a weak base ionizes. The OH\(^{-}\) and CH\(_3\)NH\(_3\)^{+} ions are equal in concentration and small amounts because they come from the weak base:

\[
\text{H}_2\text{O} > \text{CH}_3\text{NH}_2 > \text{OH}^- = \text{CH}_3\text{NH}_3^+
\]

13.143 Answer: E; HF is the strongest acid because it has the greatest \(K_a\) value, indicating that HF ionizes more completely than the other acids; CH\(_3\)CO\(_2\)H is the most concentrated acid because it has the greatest molarity (M) value.

HOCl is the weakest acid because it has the smallest \(K_a\) value; HF is the least concentrated because it has the lowest molar concentration.

13.144 Answer: D; because HF has the largest \(K_a\) value, the ionization reaction goes further to the right. Therefore HF ionizes to the greatest extent.

The greater the \(K_a\) value, the greater the extent of acid ionization: NH\(_4\)^{+} < HCN < HNO\(_2\) < HF

13.145 Answer: C; the equation \(pH = -\log[H_3O^+]\) tells us that the greater the concentration of H\(_3O^+\), the lower the pH. Bases generate OH\(^{-}\), not H\(_3O^+\). When comparing equal concentrations of strong and weak acids, the strong acids generate a higher concentration of H\(_3O^+\). Of the substances listed, HCl is the only strong acid, so it would have the lowest pH.

The solutions containing a base (0.2 \(M\) NaOH and 0.2 \(M\) NH\(_3\)) should have a pH above 7 because they have a greater [OH\(^{-}\)], and therefore a lower [H\(_3O^+\)], than neutral water.

13.146 Answer: A; a basic solution has a pH greater than 7, a concentration of OH\(^{-}\) greater than 1.0 × 10\(^{-7}\) \(M\), and a H\(_3O^+\) concentration less than 1.0 × 10\(^{-7}\) \(M\).

E. In a neutral solution, [H\(_3O^+\)] = [OH\(^{-}\)] due to the self-ionization of water.

13.147 Answer: D; the concentration of the solution obtained by diluting 10.0 mL of 0.10 \(M\) HCl to a total volume of 1000.0 mL can be calculated using the equation

\[
M_1V_1 = M_2V_2
\]

\[
M_2 = \frac{M_1V_1}{V_2} = \frac{0.10M \times 10.0 \text{ mL}}{1000 \text{ mL}} = 1.0 \times 10^{-3} M \text{ HCl solution}
\]

HCl is a strong acid that ionizes completely, so [H\(_3O^+\)] = [HCl] = 1.0 × 10\(^{-3}\) \(M\)

\[
\text{pH} = -\log[H_3O^+] = -\log(1.0 \times 10^{-3}) = 3.00
\]
The 0.10 \text{M} \text{HCl} solution has a pH of 1.00 (pH = \text{-log} 0.10). Diluting this solution will cause the pH to increase, so a solution of a pH of –1.0 cannot be obtained by dilution. Diluting 10.0 mL of 0.10 \text{M} \text{HCl} to a total volume of 100.0 mL (0.1000 L) gives a solution with an \text{H}_3\text{O}^+ concentration of 1.0\times10^{-2} \text{M} and a pH of 2.00:

\[
pH = \text{-log} (1.0\times10^{-2}) = \text{-log}(1.0\times10^{-2}) = 2.00
\]

Diluting 10.0 mL of 0.10 \text{M} \text{HCl} to a total volume of 10,000.0 mL (10.0 \text{L}) gives a solution with an \text{H}_3\text{O}^+ concentration of 1.0\times10^{-4} \text{M} and a pH of 4.00:

\[
pH = \text{-log} (1.0\times10^{-4}) = \text{-log}(1.0\times10^{-4}) = 4.00
\]

Answer: D; buffers act to prevent large changes in pH by consuming most of the acid (\text{H}_3\text{O}^+) or base (\text{OH}^-) added to the equilibrium in solution. When an acid is added, the \text{H}_3\text{O}^+ concentration would increase by just a small amount, causing the pH to decrease by less than 1.0.

Without the buffer, no \text{H}_3\text{O}^+ would be consumed. The \text{H}_3\text{O}^+ concentration in the solution would increase to 0.10 \text{M}, resulting in a pH of 1.00:

\[
pH = \text{-log} [\text{H}_3\text{O}^+] = \text{-log}(0.10) = 1.00
\]