## Chapter 13 Review Questions and Text Homework Solutions

## Review Questions

2. a. The $\mathrm{K}_{\mathrm{a}}$ reaction always refers to an acid reacting with water to produce the conjugate base of the acid and the hydronium ion $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$. For a general weak acid HA , the $K_{\mathrm{a}}$ reaction is:

$$
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{A}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \text { where } \mathrm{A}^{-}=\text {conjugate base of the acid } \mathrm{HA}
$$

This reaction is often abbreviated as: $\mathrm{HA}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{A}^{-}(a q)$
b. The $K_{\mathrm{a}}$ equilibrium constant is the equilibrium constant for the $K_{\mathrm{a}}$ reaction of some substance. For the general $K_{\mathrm{a}}$ reaction, the $K_{\mathrm{a}}$ expression is:

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{A}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HA}]} \text { or } K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \text { (for the abbreviated } K_{\mathrm{a}} \text { reaction) }
$$

c. The $K_{\mathrm{b}}$ reaction always refers to a base reacting with water to produce the conjugate acid of the base and the hydroxide ion $\left(\mathrm{OH}^{-}\right)$. For a general base, B, the $K_{\mathrm{b}}$ reaction is:

$$
\mathrm{B}(a q)+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{BH}^{+}(a q)+\mathrm{OH}^{-}(a q) \text { where } \mathrm{BH}^{+}=\text {conjugate acid of the base } \mathrm{B}
$$

d. The $K_{\mathrm{b}}$ equilibrium constant for the general $K_{\mathrm{b}}$ reaction is: $K_{\mathrm{b}}=\frac{\left[\mathrm{BH}^{+}\right]\left[\mathrm{OH}^{-}\right]}{[\mathrm{B}]}$
e. A conjugate acid-base pair consists of two substances related to each other by the donating and accepting of a single proton $\left(\mathrm{H}^{+}\right)$. The conjugate bases of the acids $\mathrm{HCl}, \mathrm{HNO}_{2}$, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, and $\mathrm{H}_{2} \mathrm{SO}_{4}$ are $\mathrm{Cl}^{-}, \mathrm{NO}_{2}^{-}, \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$, and $\mathrm{HSO}_{4}^{-}$, respectively. The conjugate acids of the bases $\mathrm{NH}_{3}, \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$, and $\mathrm{HONH}_{2}$ are $\mathrm{NH}_{4}{ }^{+}, \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}$, and $\mathrm{HONH}_{3}{ }^{+}$, respectively. Conjugate acid-base pairs only differ by $\mathrm{H}^{+}$in their respective formulas.
3. a. Amphoteric: A substance that can behave either as an acid or as a base.
b. The $K_{\mathrm{w}}$ reaction is also called the autoionization of water reaction. The reaction always occurs when water is present as the solvent. The reaction is:

$$
\mathrm{H}_{2} \mathrm{O}(l)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{OH}^{-}(a q) \text { or } \mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

c. The $K_{\mathrm{w}}$ equilibrium constant is also called the ion-product constant or the dissociation constant of water. It is the equilibrium constant for the autoionization reaction of water:

$$
K_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \text {or } K_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

At typical solution temperatures of $25^{\circ} \mathrm{C}, K_{\mathrm{w}}=1.0 \times 10^{-14}$.
d. pH is a mathematical term which is equal to the $-\log$ of the $\mathrm{H}^{+}$concentration of a solution ( $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$).
e. pOH is a mathematical term which is equal to the $-\log$ of the $\mathrm{OH}^{-}$concentration of a solution ( $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$).
f. The p of any quantity is the $-\log$ of that quantity. $\mathrm{So}: \mathrm{p} K_{\mathrm{w}}=-\log K_{\mathrm{w}}$. At $25^{\circ} \mathrm{C}$, $\mathrm{p} K_{\mathrm{w}}=-\log \left(1.0 \times 10^{-14}\right)=14.00$.

Neutral solution at $25^{\circ} \mathrm{C}: K_{\mathrm{w}}=1.0 \times 10^{-14}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$and $\mathrm{pH}+\mathrm{pOH}=14.00$

$$
\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{M} ; \mathrm{pH}=\mathrm{pOH}=-\log \left(1.0 \times 10^{-7}\right)=7.00
$$

Acidic solution at $25^{\circ} \mathrm{C}$ :

$$
\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right] ;\left[\mathrm{H}^{+}\right]>1.0 \times 10^{-7} \mathrm{M} ;\left[\mathrm{OH}^{-}\right]<1.0 \times 10^{-7} \mathrm{M} ; \mathrm{pH}<7.00 ; \mathrm{pOH}>7.00
$$

Basic solution at $25^{\circ} \mathrm{C}$ :

$$
\left[\mathrm{OH}^{-}\right]>\left[\mathrm{H}^{+}\right] ;\left[\mathrm{OH}^{-}\right]>1.0 \times 10^{-7} \mathrm{M} ;\left[\mathrm{H}^{+}\right]<1.0 \times 10^{-7} M ; \mathrm{pOH}<7.00 ; \mathrm{pH}>7.00
$$

As a solution becomes more acidic, $\left[\mathrm{H}^{+}\right]$increases, so $\left[\mathrm{OH}^{-}\right]$decreases, pH decreases, and pOH increases. As a solution becomes more basic, $\left[\mathrm{OH}^{-}\right]$increases, so $\left[\mathrm{H}^{+}\right]$decreases, pH increases, and pOH decreases.
4. The $K_{\mathrm{a}}$ value refers to the reaction of an acid reacting with water to produce the conjugate base and $\mathrm{H}_{3} \mathrm{O}^{+}$. The stronger the acid, the more conjugate base and $\mathrm{H}_{3} \mathrm{O}^{+}$produced, and the larger the $K_{\mathrm{a}}$ value.

Strong acids are basically $100 \%$ dissociated in water. Therefore, the strong acids have a $K_{\mathrm{a}} \gg 1$ because the equilibrium position lies far to the right. The conjugate bases of strong acids are terrible bases; much worse than water, so we can ignore their basic properties in water.

Weak acids are only partially dissociated in water. We say that the equilibrium lies far to the left, thus giving values for $K_{\mathrm{a}}<1$ (weak acids have mostly reactants at equilibrium and few products present). The conjugate bases of weak acids are better bases than water. When we have a solution composed of just the conjugate base of a weak acid in water, the resulting pH is indeed basic ( pH $>7.0$ ). In general, as the acid strength increases, the conjugate base strength decreases, or as acid strength decreases, the conjugate base strength increases. They are inversely related.

Base strength is directly related to the $K_{\mathrm{b}}$ value. The larger the $K_{\mathrm{b}}$ value, the more $\mathrm{OH}^{-}$produced from the $K_{\mathrm{b}}$ reaction, and the more basic the solution (the higher the pH ). Weak bases have a $K_{\mathrm{b}}$ < 1 and their conjugate acids behave as weak acids in solution. As the strength of the base increases, the strength of the conjugate acid gets weaker; the stronger the base, the weaker the conjugate acid, or the weaker the base, the stronger the conjugate acid.
5. Strong acids are assumed $100 \%$ dissociated in water, and we assume that the amount of $\mathrm{H}^{+}$donated by water is negligible. Hence, the equilibrium $\left[\mathrm{H}^{+}\right]$of a strong acid is generally equal to the initial acid concentration ( $[\mathrm{HA}]_{0}$ ). Note that solutions of $\mathrm{H}_{2} \mathrm{SO}_{4}$ can be different from this because $\mathrm{H}_{2} \mathrm{SO}_{4}$ is a diprotic acid. Also, when you have very dilute solutions of a strong acid, the $\mathrm{H}^{+}$contribution from water by itself must be considered. The strong acids to memorize are $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}$, $\mathrm{HClO}_{4}$, and $\mathrm{H}_{2} \mathrm{SO}_{4}$.
$K_{\mathrm{a}}$ values for weak acids are listed in Table 13.2 and in Appendix 5 of the text. Because weak acids only partially dissociate in water, we must solve an equilibrium problem to determine how much $\mathrm{H}^{+}$is added to water by the weak acid. We write down the $K_{\mathrm{a}}$ reaction, set-up the ICE table, then solve the equilibrium problem. The two assumptions generally made are that acids are less than 5\% dissociated in water and that the $\mathrm{H}^{+}$contribution from water is negligible.

The 5\% rule comes from the assumptions that weak acids are less than $5 \%$ dissociated. When this is true, the mathematics of the problem are made much easier. The equilibrium expression we get for weak acids in water generally has the form (assuming an initial acid concentration of 0.10 M ):

$$
K_{\mathrm{a}}=\frac{x^{2}}{0.10-x} \approx \frac{x^{2}}{0.10}
$$

The $5 \%$ rule refers to assuming $0.10-x \approx 0.10$. The assumption is valid if $x$ is less than $5 \%$ of the number the assumption was made against ( $[\mathrm{HA}]_{0}$ ). When the $5 \%$ rule is valid, solving for $x$ is very straight forward. When the $5 \%$ rule fails, we must solve the mathematical expression exactly using the quadratic equation (or your graphing calculator). Even if you do have a graphing calculator, reference Appendix 1 to review the quadratic equation. Appendix 1 also discusses the method of successive approximations which can also be used to solve quadratic (and cubic) equations.
6. Strong bases are soluble ionic compounds containing the $\mathrm{OH}^{-}$anion. Strong bases increase the $\mathrm{OH}^{-}$ concentration in water by just dissolving. Thus, for strong bases like $\mathrm{LiOH}, \mathrm{NaOH}, \mathrm{KOH}, \mathrm{RbOH}$, and CsOH , the initial concentration of the strong base equals the equilibrium $\left[\mathrm{OH}^{-}\right]$of water.

The other strong bases to memorize have +2 charged metal cations. The soluble ones to know are $\mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{Sr}(\mathrm{OH})_{2}$, and $\mathrm{Ba}(\mathrm{OH})_{2}$. These are slightly more difficult to solve because they donate 2 moles $\mathrm{OH}^{-}$for every mole of salt dissolved. Here, the $\left[\mathrm{OH}^{-}\right]$is equal to two times the initial concentration of the soluble alkaline earth hydroxide salt dissolved.
Neutrally charged organic compounds containing at least one nitrogen atom generally behave as weak bases. The nitrogen atom has an unshared pair of electrons around it. This lone pair of electrons is used to form a bond to $\mathrm{H}^{+}$.

Weak bases only partially react with water to produce $\mathrm{OH}^{-}$. To determine the amount of $\mathrm{OH}^{-}$ produced by the weak base (and, in turn, the pH of the solution), we set-up the ICE table using the $K_{\mathrm{b}}$ reaction of the weak base. The typical weak base equilibrium expression is:

$$
\left.K_{\mathrm{b}}=\frac{x^{2}}{0.25-x} \approx \frac{x^{2}}{0.25} \quad \text { (assuming }[\mathrm{B}]_{0}=0.25 \mathrm{M}\right)
$$

Solving for $x$ gives us the $\left[\mathrm{OH}^{-}\right]$in solution. We generally assume that weak bases are less than $5 \%$ reacted with water and that the $\mathrm{OH}^{-}$contribution from water is negligible. The $5 \%$ assumption makes the math easier. By assuming an expression like $0.25 M-x \approx 0.25 M$, the calculation is very straight forward. The $5 \%$ rule applied here is that if $(x / 0.25) \times 100$ is less than $5 \%$, the assumption is valid. When the assumption is not valid, then we solve the equilibrium expression exactly using the quadratic equation (or by the method of successive approximations).
7. Monoprotic acid: An acid with one acidic proton; the general formula for monoprotic acids is HA.

Diprotic acid: An acid with two acidic protons $\left(\mathrm{H}_{2} \mathrm{~A}\right)$.
Triprotic acid: An acid with three acidic protons $\left(\mathrm{H}_{3} \mathrm{~A}\right)$.

$$
\begin{array}{ll}
\mathrm{H}_{2} \mathrm{SO}_{4}(a q) \rightarrow \mathrm{HSO}_{4}^{-}(a q)+\mathrm{H}^{+}(a q) & K_{\mathrm{a}_{1}} \gg 1 ; \text { this is a strong acid. } \\
\mathrm{HSO}_{4}^{-}(a q) \rightleftharpoons \mathrm{SO}_{4}^{2-}(a q)+\mathrm{H}^{+}(a q) & K_{\mathrm{a}_{2}}=0.012 ; \text { this is a weak acid. }
\end{array}
$$

When $\mathrm{H}_{2} \mathrm{SO}_{4}$ is dissolved in water, the first proton is assumed $100 \%$ dissociated because $\mathrm{H}_{2} \mathrm{SO}_{4}$ is a strong acid. After $\mathrm{H}_{2} \mathrm{SO}_{4}$ dissociates, we have $\mathrm{H}^{+}$and $\mathrm{HSO}_{4}^{-}$present. $\mathrm{HSO}_{4}^{-}$is a weak acid and can donate some more protons to water. To determine the amount of $\mathrm{H}^{+}$donated by $\mathrm{HSO}_{4}^{-}$, one must solve an equilibrium problem using the $K_{\mathrm{a}_{2}}$ reaction for $\mathrm{HSO}_{4}{ }^{-}$.

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{PO}_{4}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(a q) \\
& \mathrm{H}_{2} \mathrm{PO}_{4}^{-}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{HPO}_{4}^{2-}(a q) \\
& \mathrm{HPO}_{4}^{2-}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{PO}_{4}^{3-}(a q)
\end{aligned}
$$

$$
\begin{aligned}
& K_{\mathrm{a}_{1}}=7.5 \times 10^{-3} \\
& K_{\mathrm{a}_{2}}=6.2 \times 10^{-8} \\
& \quad K_{\mathrm{a}_{3}}=4.8 \times 10^{-13}
\end{aligned}
$$

When $\mathrm{H}_{3} \mathrm{PO}_{4}$ is added to water, the three acids that are present are $\mathrm{H}_{3} \mathrm{PO}_{4}, \mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$, and $\mathrm{HPO}_{4}{ }^{2-}$. $\mathrm{H}_{3} \mathrm{PO}_{4}$, with the largest $K_{\mathrm{a}}$ value, is the strongest of these weak acids. The conjugate bases of the three acids are $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}, \mathrm{HPO}_{4}{ }^{2-}$, and $\mathrm{PO}_{4}{ }^{3-}$. Because $\mathrm{HPO}_{4}{ }^{2-}$ is the weakest acid (smallest $K_{\mathrm{a}}$ value), its conjugate base $\left(\mathrm{PO}_{4}{ }^{3-}\right)$ will have the largest $K_{\mathrm{b}}$ value and is the strongest base.

See Examples 13.15-13.17 of the text on the strategies used to solve for the pH of polyprotic acids. The strategy to solve most polyprotic acid solutions is covered in Example 13.15. For typical polyprotic acids, $K_{\mathrm{a}_{1}} \gg K_{\mathrm{a}_{2}}$ (and $K_{\mathrm{a}_{3}}$ if a triprotic acid). Because of this, the dominant producer of $\mathrm{H}^{+}$in solution is just the $K_{\mathrm{a}_{1}}$ reaction. We set-up the equilibrium problem using the $K_{\mathrm{a}_{1}}$ reaction and solve for $\mathrm{H}^{+}$. We then assume that the $\mathrm{H}^{+}$donated by the $K_{\mathrm{a}_{2}}$ (and $K_{\mathrm{a}_{3}}$ if triprotic) reaction is negligible, that is, the $\mathrm{H}^{+}$donated by the $K_{\mathrm{a}_{1}}$ reaction is assumed to be the $\mathrm{H}^{+}$donated by the entire acid system. This assumption is great when $K_{\mathrm{a}_{1}} \gg K_{\mathrm{a}_{2}}$ (roughly a 1000 fold difference in magnitude).

Examples 13.16 and 13.17 cover strategies for the other type of polyprotic acid problems. This other type is solutions of $\mathrm{H}_{2} \mathrm{SO}_{4}$. As discussed previously, $\mathrm{H}_{2} \mathrm{SO}_{4}$ problems are both a strong acid and a weak acid problem in one. To solve for the $\left[\mathrm{H}^{+}\right]$, we sometimes must worry about the $\mathrm{H}^{+}$ contribution from $\mathrm{HSO}_{4}{ }^{-}$. Example 13.16 is an example of an $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution where the $\mathrm{HSO}_{4}^{-}$ contribution of $\mathrm{H}^{+}$can be ignored. Example 13.17 illustrates an $\mathrm{H}_{2} \mathrm{SO}_{4}$ problem where we can't ignore the $\mathrm{H}^{+}$contribution from $\mathrm{HSO}_{4}^{-}$.
8. a. $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$
b. An acid-base reaction can be thought of as a competition between two opposing bases. Since this equilibrium lies far to the left $\left(K_{\mathrm{a}}<1\right), \mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$is a stronger base than $\mathrm{H}_{2} \mathrm{O}$.
c. The acetate ion is a better base than water and produces basic solutions in water. When we put acetate ion into solution as the only major basic species, the reaction is:

$$
\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-}
$$

Now the competition is between $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$and $\mathrm{OH}^{-}$for the proton. Hydroxide ion is the strongest base possible in water. The equilibrium above lies far to the left, resulting in a $K_{\mathrm{b}}$ value less than one. Those species we specifically call weak bases ( $10^{-14}<K_{\mathrm{b}}<1$ ) lie between $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{OH}^{-}$in base strength. Weak bases are stronger bases than water but are weaker bases than $\mathrm{OH}^{-}$.

The $\mathrm{NH}_{4}{ }^{+}$ion is a weak acid because it lies between $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{H}_{3} \mathrm{O}^{+}\left(\mathrm{H}^{+}\right)$in terms of acid strength. Weak acids are better acids than water, thus their aqueous solutions are acidic. They are weak acids because they are not as strong as $\mathrm{H}_{3} \mathrm{O}^{+}\left(\mathrm{H}^{+}\right)$. Weak acids only partially dissociate in water and have $K_{\mathrm{a}}$ values between $10^{-14}$ and 1 .

For a strong acid HX having $K_{\mathrm{a}}=1 \times 10^{6}$, the conjugate base, $\mathrm{X}^{-}$, has $K_{\mathrm{b}}=K_{\mathrm{w}} / K_{\mathrm{a}}$ $=1.0 \times 10^{-14} / 1 \times 10^{6}=1 \times 10^{-20}$ (a very small value).

The conjugate bases of strong acids have extremely small values for $K_{\mathrm{b}}$; so small that they are worse bases than water ( $K_{\mathrm{b}} \ll K_{\mathrm{w}}$ ). Therefore, conjugate bases of strong acids have no basic properties in water. They are present, but they only balance charge in solution and nothing else. The conjugate bases of the six strong acids are $\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{I}^{-}, \mathrm{NO}_{3}^{-}, \mathrm{ClO}_{4}^{-}$, and $\mathrm{HSO}_{4}^{-}$.

Summarizing the acid-base properties of conjugates:
a. The conjugate base of a weak acid is a weak base $\left(10^{-14}<K_{\mathrm{b}}<1\right)$
b. The conjugate acid of a weak base is a weak acid $\left(10^{-14}<K_{\mathrm{a}}<1\right)$
c. The conjugate base of a strong acid is a worthless base ( $K_{\mathrm{b}} \ll 10^{-14}$ )
d. The conjugate acid of a strong base is a worthless acid $\left(K_{\mathrm{a}} \ll 10^{-14}\right)$

Identifying/recognizing the acid-base properties of conjugates is crucial in order to understand the acid-base properties of salts. The salts we will give you will be salts containing the conjugates discussed above. Your job is to recognize the type of conjugate present, and then use that information to solve an equilibrium problem (if necessary).
9. A salt is an ionic compound composed of a cation and an anion.

Weak base anions: These are the conjugate bases of the weak acids having the HA general formula. Table 13.2 of the text lists several HA type acids. Some weak base anions derived from the acids in Table 13.2 are $\mathrm{ClO}_{2}^{-}, \mathrm{F}^{-}, \mathrm{NO}_{2}^{-}, \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}, \mathrm{OCl}^{-}$, and $\mathrm{CN}^{-}$.

Garbage anions (those anions with no basic or acidic properties): These are the conjugate bases of the strong acids having the HA general formula. These are $\mathrm{Cl}^{-}, \mathrm{NO}_{3}^{-}, \mathrm{Br}^{-}, \mathrm{I}^{-}$, and $\mathrm{ClO}_{4}^{-}$.

Weak acid cations: These are the conjugate acids of the weak bases which contain nitrogen. Table 13.3 of the text lists several nitrogen-containing bases. Some weak acid cations derived from the weak bases in Table 13.3 are $\mathrm{NH}_{4}{ }^{+}, \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}, \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}$, and $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}$.

Garbage cations (those cations with no acidic properties or basic properties): The most common ones used are the cations in the strong bases. These are $\mathrm{Li}^{+}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Rb}^{+}, \mathrm{Cs}^{+}, \mathrm{Ca}^{2+}, \mathrm{Sr}^{2+}$, and $\mathrm{Ba}^{2+}$.

We mix and match the cations and anions to get what type of salt we want. For a weak base salt, we combine a weak base anion with a garbage cation. Some weak base salts are $\mathrm{NaF}, \mathrm{KNO}_{2}$, $\mathrm{Ca}(\mathrm{CN})_{2}$, and $\mathrm{RbC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$. To determine the pH of a weak base salt, we write out the $K_{\mathrm{b}}$ reaction for the weak base anion and determine $K_{\mathrm{b}}\left(=K_{\mathrm{w}} / K_{\mathrm{a}}\right)$. We set up the ICE table under the $K_{\mathrm{b}}$ reaction, and then solve the equilibrium problem to calculate $\left[\mathrm{OH}^{-}\right]$and, in turn, pH .

For a weak acid salt, we combine a weak acid cation with a garbage anion. Some weak acid salts are $\mathrm{NH}_{4} \mathrm{Cl}, \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NHNO}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{I}$, and $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3} \mathrm{ClO}_{4}$. To determine the pH , we write out the $K_{\mathrm{a}}$ reaction for the weak acid cation and determine $K_{\mathrm{a}}\left(=K_{\mathrm{w}} / K_{\mathrm{b}}\right)$. We set up the ICE table under the $K_{\mathrm{a}}$ reaction, and then solve the equilibrium problem to calculate $\left[\mathrm{H}^{+}\right]$and, in turn, pH .

For a neutral ( $\mathrm{pH}=7.0$ ) salt, we combine a garbage cation with a garbage anion. Some examples are $\mathrm{NaCl}, \mathrm{KNO}_{3}, \mathrm{BaBr}_{2}$, and $\mathrm{Sr}\left(\mathrm{ClO}_{4}\right)_{2}$.

For salts that contain a weak acid cation and a weak base anion, we compare the $K_{\mathrm{a}}$ value of the weak acid cation to the $K_{\mathrm{b}}$ value for the weak base anion. When $K_{\mathrm{a}}>K_{\mathrm{b}}$, the salt produces an acidic solution ( $\mathrm{pH}<7.0$ ). When $K_{\mathrm{b}}>K_{\mathrm{a}}$, the salt produces a basic solution. And when $K_{\mathrm{a}}=K_{\mathrm{b}}$, the salt produces a neutral solution ( $\mathrm{pH}=7.0$ ).

## Text Homework

20. Acidic solutions (at $25^{\circ} \mathrm{C}$ ) have an $\left[\mathrm{H}^{+}\right]>1.0 \times 10^{-7} \mathrm{M}$, which gives a pH $<7.0$. Because $\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$ $=1.0 \times 10^{-14}$ and $\mathrm{pH}+\mathrm{pOH}=14.00$ for an aqueous solution at $25^{\circ} \mathrm{C}$, an acidic solution must also have $\left[\mathrm{OH}^{-}\right]<1.0 \times 10^{-7} \mathrm{M}$ and $\mathrm{pOH}>7.00$. From these relationships, the solutions in parts $\mathrm{a}, \mathrm{b}$, and d are acidic. The solution in part c will have a $\mathrm{pH}>7.0(\mathrm{pH}=14.00-4.51=9.49)$ and is therefore not acidic (solution is basic).
21. Only statement a is true (assuming the species is not amphoteric). You cannot add a base to water and get an acidic $\mathrm{pH}(\mathrm{pH}<7.0)$. For statement b, you can have negative pH values; this just indicates an $\left[\mathrm{H}^{+}\right]>1.0 \mathrm{M}$. For statement c , a dilute solution of a strong acid can have a higher pH than a more concentrated weak acid solution. For statement d, the $\mathrm{Ba}(\mathrm{OH})_{2}$ solution will have an $\left[\mathrm{OH}^{-}\right]$twice of the same concentration of KOH , but this does not correspond to a pOH value twice that of the same concentration of KOH (prove it to yourselves).
22. $\mathrm{H}_{2} \mathrm{CO}_{3}$ is a weak acid with $\mathrm{K}_{\mathrm{a}_{1}}=4.3 \times 10^{-7}$ and $\mathrm{K}_{\mathrm{a}_{2}}=5.6 \times 10^{-11}$. The $\left[\mathrm{H}^{+}\right]$concentration in solution will be determined from the $\mathrm{K}_{\mathrm{a}_{1}}$ reaction because $\mathrm{K}_{\mathrm{a}_{1}} \gg \mathrm{~K}_{\mathrm{a}_{2}}$. Because $\mathrm{K}_{\mathrm{a}_{1}} \ll 1$, the $\left[\mathrm{H}^{+}\right]$ $<0.10 \mathrm{M}$; only a small percentage of the $0.10 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}$ will dissociate into $\mathrm{HCO}_{3}{ }^{-}$and $\mathrm{H}^{+}$. So statement a best describes the $0.10 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}$ solution. $\mathrm{H}_{2} \mathrm{SO}_{4}$ is a strong acid as well as a very good weak acid ( $\mathrm{K}_{\mathrm{a}_{1}} \gg 1, \mathrm{~K}_{\mathrm{a}_{2}}=1.2 \times 10^{-2}$ ). All the $0.10 \mathrm{MH}_{2} \mathrm{SO}_{4}$ solution will dissociate into 0.10 $M \mathrm{H}^{+}$and $0.10 \mathrm{M} \mathrm{HSO}_{4}^{-}$. However, because $\mathrm{HSO}_{4}^{-}$is a good weak acid due to the relatively large $\mathrm{K}_{\mathrm{a}}$ value, some of the $0.10 \mathrm{M} \mathrm{HSO}_{4}{ }^{-}$will dissociate into some more $\mathrm{H}^{+}$and $\mathrm{SO}_{4}{ }^{2-}$. Therefore, the $\left[\mathrm{H}^{+}\right.$] will be greater than 0.10 M but will not reach 0.20 M because only some of $0.10 \mathrm{M} \mathrm{HSO}_{4}{ }^{-}$will dissociate. Statement c is best for a $0.10 \mathrm{M}_{2} \mathrm{SO}_{4}$ solution.
23. a. Sulfur reacts with oxygen to produce $\mathrm{SO}_{2}$ and $\mathrm{SO}_{3}$. These sulfur oxides both react with water to produce $\mathrm{H}_{2} \mathrm{SO}_{3}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$, respectively. Acid rain can result when sulfur emissions are not controlled. Note that, in general, nonmetal oxides react with water to produce acidic solutions.
b. CaO reacts with water to produce $\mathrm{Ca}(\mathrm{OH})_{2}$, a strong base. A gardener mixes lime $(\mathrm{CaO})$ into soil in order to raise the pH of the soil. The effect of adding lime is to add $\mathrm{Ca}(\mathrm{OH})_{2}$. Note that, in general, metal oxides react with water to produce basic solutions.
24. The beaker on the left represents a strong acid in solution; the acid HA is $100 \%$ dissociated into the $\mathrm{H}^{+}$and $\mathrm{A}^{-}$ions. The beaker on the right represents a weak acid in solution; only a little bit of the acid HB dissociates into ions, so the acid exists mostly as undissociated HB molecules in water.
a. $\mathrm{HNO}_{2}$ : weak acid beaker
b. $\mathrm{HNO}_{3}$ : strong acid beaker
c. HCl: strong acid beaker
d. HF: weak acid beaker
e. $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ : weak acid beaker
25. a. $\left[\mathrm{H}^{+}\right]=\frac{\mathrm{K}_{\mathrm{w}}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{1.5}=6.7 \times 10^{-15} \mathrm{M}$; basic
b. $\quad\left[\mathrm{H}^{+}\right]=\frac{1.0 \times 10^{-14}}{3.6 \times 10^{-15}}=2.8 \mathrm{M}$; acidic
c. $\quad\left[\mathrm{H}^{+}\right]=\frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}}=1.0 \times 10^{-7} \mathrm{M}$; neutral
d. $\left[\mathrm{H}^{+}\right]=\frac{1.0 \times 10^{-14}}{7.3 \times 10^{-4}}=1.4 \times 10^{-11} \mathrm{M}$; basic
26. $\mathrm{pH}=14.00-\mathrm{pOH}=14.00-5.74=8.26 ;\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}}=10^{-8.26}=5.5 \times 10^{-9} \mathrm{M}$
$\left[\mathrm{OH}^{-}\right]=\frac{\mathrm{K}_{\mathrm{w}}}{\left[\mathrm{H}^{+}\right]}=\frac{1.0 \times 10^{-14}}{5.5 \times 10^{-9}}=1.8 \times 10^{-6} \mathrm{M}$ or $\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}=10^{-5.74}=1.8 \times 10^{-6} \mathrm{M}$
The solution of baking soda is basic because the pH is greater than 7.00 at $25^{\circ} \mathrm{C}$.
27. a. $\mathrm{HOC}_{6} \mathrm{H}_{5}\left(\mathrm{~K}_{\mathrm{a}}=1.6 \times 10^{-10}\right)$ and $\mathrm{H}_{2} \mathrm{O}\left(\mathrm{K}_{\mathrm{a}}=\mathrm{K}_{\mathrm{w}}=1.0 \times 10^{-14}\right)$ are the major species. The major equilibrium is the dissociation of $\mathrm{HOC}_{6} \mathrm{H}_{5}$. Solving the weak acid problem:

|  | $\mathrm{HOC}_{6} \mathrm{H}_{5}$ | $\rightleftharpoons$ | $\mathrm{H}^{+}$ | + |
| :--- | :---: | :---: | :---: | :---: |
| Initial | 0.250 M | $\mathrm{OC}_{6} \mathrm{H}_{5}{ }^{-}$ |  |  |
|  | $x \mathrm{~mol} / \mathrm{L} \mathrm{HOC}_{6} \mathrm{H}_{5}$ dissociates to reach equilibrium |  |  |  |
| Change | $-x$ | $\rightarrow$ | $+x$ | $+x$ |
| Equil. | $0.250-x$ | $x$ | $x$ |  |
| $\mathrm{~K}_{\mathrm{a}}=1.6 \times 10^{-10}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OC}_{6} \mathrm{H}_{5}{ }^{-}\right]}{\left[\mathrm{HOC}_{6} \mathrm{H}_{5}\right]}=\frac{x^{2}}{0.250-x} \approx \frac{x^{2}}{0.250}$ (assuming $x \ll 0.250$ ) |  |  |  |  |

$x=\left[\mathrm{H}^{+}\right]=6.3 \times 10^{-6} M$; checking assumption: $x$ is $2.5 \times 10^{-3} \%$ of 0.250 , so assumption is valid by the $5 \%$ rule.
$\mathrm{pH}=-\log \left(6.3 \times 10^{-6}\right)=5.20$
b. $\mathrm{HCN}\left(\mathrm{K}_{\mathrm{a}}=6.2 \times 10^{-10}\right)$ and $\mathrm{H}_{2} \mathrm{O}$ are the major species. HCN is the major source of $\mathrm{H}^{+}$.

|  | HCN | $\rightleftharpoons$ | $\mathrm{H}^{+}$ | + |
| :--- | :---: | :---: | :---: | :---: |
| Initial | 0.250 M | $\sim 0$ | $\mathrm{CN}^{-}$ |  |
|  | $x \mathrm{~mol} / \mathrm{L}$ HCN dissociates to reach equilibrium |  |  |  |
| Change | $-x$ | $\rightarrow$ | $+x$ | $+x$ |
| Equil. | $0.250-x$ | $x$ | $x$ |  |

$\mathrm{K}_{\mathrm{a}}=6.2 \times 10^{-10}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CN}^{-}\right]}{[\mathrm{HCN}]}=\frac{x^{2}}{0.250-x} \approx \frac{x^{2}}{0.250} \quad$ (assuming $x \ll 0.250$ )
$x=\left[\mathrm{H}^{+}\right]=1.2 \times 10^{-5} \mathrm{M}$; checking assumption: $x$ is $4.8 \times 10^{-3} \%$ of 0.250 .
Assumptions good. $\mathrm{pH}=-\log \left(1.2 \times 10^{-5}\right)=4.92$
76.

|  | HX | $\rightleftharpoons$ | $\mathrm{H}^{+}$ | X | where $\mathrm{I}=[\mathrm{HX}]_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Initial | $\underset{x}{\text { mol/L }} \mathrm{HX}$ dissociates to reach equilibrium |  |  |  |  |
|  |  |  |  |  |  |
| Change | -x | $\rightarrow$ | $+x$ | + $\chi$ |  |
| Equil. | I - $x$ |  | $x$ | $x$ |  |

From the problem, $x=0.25$ (I) and $\mathrm{I}-x=0.30 \mathrm{M}$.
$\mathrm{I}-0.25(\mathrm{I})=0.30 \mathrm{M}, \mathrm{I}=0.40 \mathrm{M}$ and $x=0.25(0.40 \mathrm{M})=0.10 \mathrm{M}$
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{X}^{-}\right]}{[\mathrm{HX}]}=\frac{x^{2}}{\mathrm{I}-\mathrm{x}}=\frac{(0.10)^{2}}{0.30}=0.033$
94. $\mathrm{pH}=10.50 ; \mathrm{pOH}=14.00-10.50=3.50 ;\left[\mathrm{OH}^{-}\right]=10^{-3.50}=3.2 \times 10^{-4} \mathrm{M}$
$\mathrm{Sr}(\mathrm{OH})_{2}(\mathrm{aq}) \rightarrow \mathrm{Sr}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq}) ; \mathrm{Sr}(\mathrm{OH})_{2}$ donates $2 \mathrm{~mol} \mathrm{OH}^{-}$per mol $\mathrm{Sr}(\mathrm{OH})_{2}$.
$\left[\mathrm{Sr}(\mathrm{OH})_{2}\right]=\frac{3.2 \times 10^{-4} \mathrm{~mol} \mathrm{OH}-}{\mathrm{L}} \times \frac{1 \mathrm{~mol} \mathrm{Sr}(\mathrm{OH})_{2}}{2 \mathrm{~mol} \mathrm{OH}^{-}}=1.6 \times 10^{-4} \mathrm{M} \mathrm{Sr}(\mathrm{OH})_{2}$
A $1.6 \times 10^{-4} \mathrm{M} \mathrm{Sr}(\mathrm{OH})_{2}$ solution will produce a $\mathrm{pH}=10.50$ solution.
104.

$$
\mathrm{HONH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HONH}_{3}^{+}+\mathrm{OH}^{-} \quad \mathrm{K}_{\mathrm{b}}=1.1 \times 10^{-8}
$$

$$
\text { Initial } \begin{array}{ccccc}
\mathrm{I} & 0 & \sim 0 & \mathrm{I}=\left[\mathrm{HONH}_{2}\right]_{0}
\end{array}
$$

Equil. I $-x$
$x \quad x$
$\mathrm{K}_{\mathrm{b}}=1.1 \times 10^{-8}=\frac{x^{2}}{\mathrm{I}-x}$
From problem, $\mathrm{pH}=10.00$, so $\mathrm{pOH}=4.00$ and $x=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-4} \mathrm{M}$.
$1.1 \times 10^{-8}=\frac{\left(1.0 \times 10^{-4}\right)^{2}}{\mathrm{I}-\left(1.0 \times 10^{-4}\right)}, \quad \mathrm{I}=0.91 \mathrm{M}$
Mass $\mathrm{HONH}_{2}=0.2500 \mathrm{~L} \times \frac{0.91 \mathrm{~mol} \mathrm{HONH}_{2}}{\mathrm{~L}} \times \frac{33.03 \mathrm{~g} \mathrm{HONH}_{2}}{\mathrm{~mol} \mathrm{HONH}} 2 \mathrm{~F}, 7.5 \mathrm{~g} \mathrm{HONH}_{2}$
106.

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) & \mathrm{K}_{\mathrm{a}_{1}}=\frac{\left[\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}\right]} \\
\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{2-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) & \mathrm{K}_{\mathrm{a}_{2}}=\frac{\left[\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{2-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}\right]} \\
\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{2-}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{3-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) & \mathrm{K}_{\mathrm{a}_{3}}=\frac{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{3-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{2-}\right]}
\end{array}
$$

116. Because $\mathrm{NH}_{3}$ is a weaker base (smaller $\mathrm{K}_{\mathrm{b}}$ value) than $\mathrm{CH}_{3} \mathrm{NH}_{2}$, the conjugate acid of $\mathrm{NH}_{3}$ will be a stronger acid than the conjugate acid of $\mathrm{CH}_{3} \mathrm{NH}_{2}$. Thus $\mathrm{NH}_{4}{ }^{+}$is a stronger acid than $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$.
117. $\quad \mathrm{BHCl} \rightarrow \mathrm{BH}^{+}+\mathrm{Cl}^{-} ; \mathrm{Cl}^{-}$is the conjugate base of the strong acid HCl , so $\mathrm{Cl}^{-}$has no acidic/ basic properties. $\mathrm{BH}^{+}$is a weak acid because it is the conjugate acid of a weak base B. Determining the $\mathrm{K}_{\mathrm{a}}$ value for $\mathrm{BH}^{+}$:

$$
\mathrm{BH}^{+} \quad \rightleftharpoons \quad \mathrm{B} \quad+\quad \mathrm{H}^{+}
$$

Initial $0.10 \mathrm{M} \quad 0 \quad \sim 0$ $x \mathrm{~mol} / \mathrm{L} \mathrm{BH}^{+}$dissociates to reach equilibrium
$\begin{array}{lllrr}\text { Change } & -x & \rightarrow & +x & +x \\ \text { Equil. } & 0.10-x & & x & x\end{array}$
$\mathrm{K}_{\mathrm{a}}=\frac{[\mathrm{B}]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{BH}^{+}\right]}=\frac{x^{2}}{0.10-x}$; from the problem, $\mathrm{pH}=5.82$ :

$$
\left[\mathrm{H}^{+}\right]=x=10^{-5.82}=1.5 \times 10^{-6} M ; \quad \mathrm{K}_{\mathrm{a}}=\frac{\left(1.5 \times 10^{-6}\right)^{2}}{0.10-\left(1.5 \times 10^{-6}\right)}=2.3 \times 10^{-11}
$$

$\mathrm{K}_{\mathrm{b}}$ for the base $\mathrm{B}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a}}=\left(1.0 \times 10^{-14}\right) /\left(2.3 \times 10^{-11}\right)=4.3 \times 10^{-4}$.
From Table 13.3 of the text, this $\mathrm{K}_{\mathrm{b}}$ value is closest to $\mathrm{CH}_{3} \mathrm{NH}_{2}$, so the unknown salt is $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$.
136. a. Basic; $\mathrm{Li}_{2} \mathrm{O}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow 2 \mathrm{LiOH}(\mathrm{aq})$; LiOH is a strong base.
b. Acidic; $\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) ; \mathrm{H}_{2} \mathrm{CO}_{3}$ is a weak diprotic acid.
c. Basic; $\mathrm{SrO}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Sr}(\mathrm{OH})_{2}(\mathrm{aq}) ; \mathrm{Sr}(\mathrm{OH})_{2}$ is a strong base.
144. Conjugate acid-base pairs differ by an $\mathrm{H}^{+}$in the formula. Pairs in parts $\mathrm{a}, \mathrm{c}$, and d are conjugate acid-base pairs. For part b, $\mathrm{HSO}_{4}^{-}$is the conjugate base of $\mathrm{H}_{2} \mathrm{SO}_{4}$. In addition, $\mathrm{HSO}_{4}^{-}$is the conjugate acid of $\mathrm{SO}_{4}{ }^{2-}$.

