### 8.1 Introduction to Acids and Bases

Essential knowledge statements from the AP Chemistry CED:

- The concentrations of hydronium ion and hydroxide ion are often reported as pH and pOH , respectively.
- $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
- $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$
- The terms "hydrogen ion" and "hydronium ion" and the symbols $\mathrm{H}^{+}(a q)$ and $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ are often used interchangeably for the aqueous ion of hydrogen. Hydronium ion and $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ are preferred, but $\mathrm{H}^{+}(a q)$ is also accepted on the AP Exam.
- Water autoionizes with an equilibrium constant $K_{w}$.
- $K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$ at $25^{\circ} \mathrm{C}$
- In pure water, $\mathrm{pH}=\mathrm{pOH}$. This is called a neutral solution.
- At $25^{\circ} \mathrm{C}, \mathrm{p} K_{w}=14.0$ and thus $\mathrm{pH}=\mathrm{pOH}=7.0$.
- $\mathrm{p} K_{w}=14=\mathrm{pH}+\mathrm{pOH}$ at $25^{\circ} \mathrm{C}$
- The value of $K_{w}$ is temperature dependent, so the pH of pure, neutral water will deviate from 7.0 at temperatures other than $25^{\circ} \mathrm{C}$.


### 4.8 Introduction to Acid-Base Reactions (Review)

Essential knowledge statements from the AP Chemistry CED:

- By definition, a Brønsted-Lowry acid is a proton donor and a Brønsted-Lowry base is a proton acceptor.
- Only in aqueous solutions, water plays an important role in many acid-base reactions, as its molecular structure allows it to accept protons from and donate protons to dissolved species.
- When an acid or base ionizes in water, the conjugate acid-base pairs can be identified and their relative strengths compared.

$$
\mathrm{HCN}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{CN}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)
$$

1. Identify both sets of conjugate acid-base pairs in the reaction above.

| Acid (Reactant) | Conjugate Base (Product) |
| :--- | :--- |
|  |  |


| Base (Reactant) | Conjugate Acid (Product) |
| :--- | :--- |
|  |  |

$$
\mathrm{CH}_{3} \mathrm{NH}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}(a q)+\mathrm{OH}^{-}(a q)
$$

2. Identify both sets of conjugate acid-base pairs in the reaction above.

| Acid (Reactant) | Conjugate Base (Product) |
| :--- | :--- |
|  |  |


| Base (Reactant) | Conjugate Acid (Product) |
| :--- | :--- |
|  |  |

In Question \#1, you observed that molecules of $\mathrm{H}_{2} \mathrm{O}$ can behave as $\mathrm{H}^{+}$acceptors (bases).
In Question \#2, you observed that molecules of $\mathrm{H}_{2} \mathrm{O}$ can behave as $\mathrm{H}^{+}$donors (acids).
The following particle diagram illustrates the process that occurs in pure water, known as the autoionization of water.


- One water molecule behaves as an acid, donating a $\mathrm{H}^{+}$ion.
- Another water molecule behaves as a base, accepting a $\mathrm{H}^{+}$ion.
- The conjugate base of $\mathrm{H}_{2} \mathrm{O}$ is the hydroxide ion, $\mathrm{OH}^{-}$.
- The conjugate acid of $\mathrm{H}_{2} \mathrm{O}$ is the hydronium ion, $\mathrm{H}_{3} \mathrm{O}^{+}$.

The chemical equation for the autoionization of water is shown below, along with the value of the equilibrium constant, $K_{w}$, at $25^{\circ} \mathrm{C}$. An alternate form of the equation is also shown in which the $\mathrm{H}_{3} \mathrm{O}^{+}$ ion is replaced with the $\mathrm{H}^{+}$ion.

$$
\begin{aligned}
2 \mathrm{H}_{2} \mathrm{O}(l) & \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{OH}^{-}(a q) & K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C} \\
\mathrm{H}_{2} \mathrm{O}(l) & \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q) & K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C}
\end{aligned}
$$

The letter " p " in symbols such as $\mathrm{pH}, \mathrm{pOH}$, and $\mathrm{p} K_{w}$ tells us to "take the negative log" of a quantity.
The concentrations for ions such as $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$in aqueous solution have units of $\mathrm{mol} / \mathrm{L}$ or $M$.
Since the $\mathrm{pH}($ or pOH$)$ is calculated from a logarithm function, the pH (or pOH ) does not have any units.
Remember that $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{H}^{+}\right]$can be used interchangeably.
If you know the value of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, you can calculate the pH of the solution as follows.

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

If you know the pH of the solution, you can calculate the value of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$as follows.

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}
$$

If you know the value of $\left[\mathrm{OH}^{-}\right]$, you can calculate the pOH of the solution as follows.

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
$$

If you know the pOH of the solution, you can calculate the value of $\left[\mathrm{OH}^{-}\right]$as follows.

$$
\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}
$$

At a temperature of $25^{\circ} \mathrm{C}$, the following relationships are true.

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \quad \mathrm{p} K_{w}=\mathrm{pH}+\mathrm{pOH}=14
$$

| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | Significant Digits | pH |
| :---: | :---: | :---: |
| $1 \times 10^{-3} \mathrm{M}$ | 1 | 3.0 |
| $1.2 \times 10^{-3} \mathrm{M}$ | 2 | 2.92 |
| $1.22 \times 10^{-3} \mathrm{M}$ | 3 | 2.914 | |  |
| :---: | | With pH (or pOH), |
| :---: |
| only the digits to the right |
| of the decimal point are |
| considered to be significant. |

3. Fill in the missing information in the tables below.

| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | pH |
| :---: | :---: |
|  | 11.65 |
|  | 6.14 |
| $4.3 \times 10^{-5} \mathrm{M}$ |  |
| 0.015 M |  |


| $\left[\mathrm{OH}^{-}\right]$ | pOH | pH |
| :---: | :---: | :---: |
|  | 10.39 |  |
|  | 8.04 |  |
| $6.8 \times 10^{-6} \mathrm{M}$ |  |  |
| $2.8 \times 10^{-4} \mathrm{M}$ |  |  |

4. As the value of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$increases, the value of pH ( decreases increases ). As the value of $\left[\mathrm{OH}^{-}\right]$increases, the value of pH ( decreases increases ).
5. Fill in the missing information in the table below. Assume that all solutions are at $25^{\circ} \mathrm{C}$.

| $\left[\mathrm{H}^{+}\right]$ | pH | $\left[\mathrm{OH}^{-}\right]$ | pOH | Acidic or Basic? |
| :---: | :---: | :---: | :---: | :---: |
| 0.075 M |  |  |  |  |
|  | 5.63 |  |  |  |
|  |  | $3.8 \times 10^{-7} \mathrm{M}$ |  |  |
|  |  |  | 4.54 |  |

$$
\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q) \quad K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C}
$$

The autoionization of water is an endothermic reaction. The value of the equilibrium constant $K_{\mathrm{w}}$ is affected by changes in temperature, as shown in the table below.

| Temperature <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $K_{\mathrm{w}}$ | $\mathrm{p} K_{w}$ | pH | pOH |
| :---: | :---: | :---: | :---: | :---: |
| 0 | $1.14 \times 10^{-15}$ | 14.943 |  |  |
| 10 | $2.93 \times 10^{-15}$ | 14.533 |  |  |
| 20 | $6.81 \times 10^{-15}$ | 14.167 |  |  |
| 25 | $1.01 \times 10^{-14}$ | 13.996 |  |  |
| 30 | $1.47 \times 10^{-14}$ | 13.833 |  |  |
| 40 | $2.92 \times 10^{-14}$ | 13.535 |  |  |
| 50 | $5.48 \times 10^{-14}$ | 13.261 |  |  |

6. In the table above, calculate the values of pH and pOH for pure water at various temperatures.
7. Decide if each of the following statements is true or false.
$\qquad$ A sample of pure $\mathrm{H}_{2} \mathrm{O}$ has a pH of 7.0 at any temperature.
$\qquad$ $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$in a sample of pure $\mathrm{H}_{2} \mathrm{O}$ at any temperature.
$\qquad$ A sample of pure $\mathrm{H}_{2} \mathrm{O}$ is neutral, in which $\mathrm{pH}=\mathrm{pOH}$.
$\qquad$ If the pH of a sample of pure $\mathrm{H}_{2} \mathrm{O}$ is less than 7 , then the temperature of the sample must be less than $25^{\circ} \mathrm{C}$.
$\qquad$ $\mathrm{H}_{2} \mathrm{O}$ ionizes to a greater extent at $50^{\circ} \mathrm{C}$ than it does at $25^{\circ} \mathrm{C}$.
$\qquad$ As the temperature increases, the pH of pure $\mathrm{H}_{2} \mathrm{O}$ decreases.
$\qquad$ If a sample of pure $\mathrm{H}_{2} \mathrm{O}$ has a pH of 6.8 , then the pOH of pure water must be 7.2.

## 8.2 pH and pOH of Strong Acids and Bases

Essential knowledge statements from the AP Chemistry CED:

- Molecules of a strong acid (e.g., $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HClO}_{4}, \mathrm{H}_{2} \mathrm{SO}_{4}$, and $\mathrm{HNO}_{3}$ ) will completely ionize in aqueous solution to produce hydronium ions. As such, the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$in a strong acid solution is equal to the initial concentration of the strong acid, and thus the pH of the strong acid solution is easily calculated.
- When dissolved in solution, strong bases (e.g., group I and II hydroxides) completely dissociate to produce hydroxide ions. As such, the concentration of $\mathrm{OH}^{-}$in a strong base solution is equal to the initial concentration of the strong base, and thus the pOH ( and pH ) of the strong base solution is easily calculated.

| Acid Name | Acid Formula | How the acid ionizes in aqueous solution |
| :---: | :---: | :---: |
| hydrochloric acid | HCl | $\mathrm{HCl}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{Cl}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| hydrobromic acid | HBr | $\mathrm{HBr}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{Br}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| hydroiodic acid | HI | $\mathrm{HI}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{I}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| perchloric acid | $\mathrm{HClO}_{4}$ | $\mathrm{HClO}_{4}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{ClO}_{4}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| nitric acid | $\mathrm{HNO}_{3}$ | $\mathrm{HNO}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{NO}_{3}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $\mathrm{H}_{2} \mathrm{SO}_{4}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{HSO}_{4}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |

The table above shows the six strong acids that you should memorize for the AP Chemistry exam. A strong acid ionizes completely in aqueous solution to produce hydronium $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$ions.
8. The following questions are related to strong acids. Assume that all solutions are at $25^{\circ} \mathrm{C}$.
(a) What is the pH of $0.050 \mathrm{MHCl}(a q)$ ? $\qquad$
(b) What is the pH of $2.5 \times 10^{-4} M \mathrm{HBr}(a q)$ ? $\qquad$
(c) What is the concentration of a solution of $\mathrm{HClO}_{4}(a q)$ if the pH is 4.25 ? $\qquad$
(d) What is the concentration of a solution of $\mathrm{HNO}_{3}(a q)$ if the pH is 6.33 ? $\qquad$

| Base Name | Base Formula | How the base dissociates in aqueous solution |
| :---: | :---: | :---: |
| sodium hydroxide | NaOH | $\mathrm{NaOH}(s) \rightleftarrows \mathrm{Na}^{+}(a q)+\mathrm{OH}^{-}(a q)$ |
| potassium hydroxide | KOH | $\mathrm{KOH}(s) \rightleftarrows \mathrm{K}^{+}(a q)+\mathrm{OH}^{-}(a q)$ |
| calcium hydroxide | $\mathrm{Ca}(\mathrm{OH})_{2}$ | $\mathrm{Ca}(\mathrm{OH})_{2}(s) \rightleftarrows \mathrm{Ca}^{2+}(a q)+2 \mathrm{OH}^{-}(a q)$ |
| strontium hydroxide | $\mathrm{Sr}(\mathrm{OH})_{2}$ | $\mathrm{Sr}(\mathrm{OH})_{2}(s) \rightleftarrows \mathrm{Sr}^{2+}(a q)+2 \mathrm{OH}^{-}(a q)$ |

The table above shows examples of group I and group II hydroxides. A strong base is an ionic solid that completely dissociates in aqueous solution to produce hydroxide $\left(\mathrm{OH}^{-}\right)$ions.
9. Fill in the missing information in the table below.

| Base | Concentration of Base | $\left[\mathrm{OH}^{-}\right]$ | pOH | pH |
| :---: | :---: | :---: | :---: | :---: |
| NaOH | 0.15 M |  |  |  |
| KOH |  |  |  | 11.51 |
| $\mathrm{Ca}(\mathrm{OH})_{2}$ | $4.7 \times 10^{-5} \mathrm{M}$ |  |  |  |
| $\mathrm{Ba}(\mathrm{OH})_{2}$ |  |  |  | 8.68 |


10. A student measures the pH of a 100.0 mL sample of $\mathrm{NaOH}(\mathrm{aq})$ and records the pH as 12.00 . Calculate the volume of distilled water that should be added to this solution so that the pH of the diluted solution is equal to 11.00 .

11. A student combined 500.0 mL of $0.050 \mathrm{M} \mathrm{HCl}(a q)$ with 500.0 mL of $0.10 \mathrm{M} \mathrm{NaOH}(a q)$ and mixed the final solution thoroughly.
(a) Write the net ionic equation for the reaction that occurs when aqueous solutions of a strong acid and a strong base are combined.
(b) Calculate the number of moles of HCl and the number of moles of NaOH present at the beginning of the experiment before the two solutions are combined.
(c) Calculate the number of moles of the excess reactant that remain left over in the combined solution. Assume that the acid-base reaction goes to completion.
(d) Calculate the pH of the combined solution at the end of the experiment.
12. The table below contains information about two solutions with the same initial concentration of acid.

| Acid | Initial Concentration <br> of Acid, HA | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$at <br> Equilibrium | pH |
| :---: | :---: | :---: | :---: |
| $\mathrm{HNO}_{3}$ | 0.036 M | 0.036 M | 1.44 |
| $\mathrm{HNO}_{2}$ | 0.036 M | 0.0036 M | 2.44 |

$$
\text { percent ionization }=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }}}{[\mathrm{HA}]_{\text {initial }}} \times 100 \%
$$

(a) Use the formula above and the data in the table to calculate the percent ionization of the acid in a solution of $0.036 \mathrm{M} \mathrm{HNO}_{3}(\mathrm{aq})$. $\qquad$
(b) Use the formula above and the data in the table to calculate the percent ionization of the acid in a solution of $0.036 M \mathrm{HNO}_{2}(\mathrm{aq})$. $\qquad$
(c) Based on your answer to part (b), explain why $\mathrm{HNO}_{2}$ is classified as a weak acid.

The particle diagram shown below should help you to compare the percent ionization for a strong acid and a weak acid.

13. The table below contains information about two solutions with the same pH . Fill in the missing information in the table below.

| Acid | Initial Concentration <br> of Acid, HA | pH | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$at <br> Equilibrium | \% Ionization <br> of the Acid |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{HNO}_{3}$ |  | 1.86 |  |  |
| $\mathrm{HNO}_{2}$ | $0.50 M$ | 1.86 |  |  |

### 8.3 Weak Acid and Base Equilibria

Essential knowledge statements from the AP Chemistry CED:

- Weak acids react with water to produce hydronium ions. However, molecules of a weak acid will only partially ionize in this way. In other words, only a small percentage of the molecules of a weak acid are ionized in a solution. Thus, the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$is much less than the initial concentration of the molecular acid, and the vast majority of the acid molecules remain un-ionized.
- A solution of a weak acid involves equilibrium between an un-ionized acid and its conjugate base. The equilibrium constant for this reaction is $K_{a}$, often reported as $\mathrm{p} K_{a}$. The pH of a weak acid solution can be determined from the initial acid concentration and the $\mathrm{p} K_{a}$.
- $K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
- $p K_{a}=-\log K_{a}$
- Weak bases react with water to produce hydroxide ions in solution. However, ordinarily just a small percentage of the molecules of a weak base in solution will ionize in this way. Thus, the concentration of $\mathrm{OH}^{-}$in the solution does not equal the initial concentration of the base, and the vast majority of the base molecules remain un-ionized.
- A solution of a weak base involves equilibrium between an un-ionized base and its conjugate acid. The equilibrium constant for this reaction is $K_{b}$, often reported as $\mathrm{p} K_{b}$. The pH of a weak base solution can be determined from the initial base concentration and the $\mathrm{p} K_{b}$.
- $K_{a}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HB}^{+}\right]}{[\mathrm{B}]}$
- $p K_{b}=-\log K_{b}$
- The percent ionization of a weak acid (or base) can be calculated from its $\mathrm{p} K_{a}\left(\mathrm{p} K_{b}\right)$ and the initial concentration of the acid (base).

| Strong Acids | Weak Acids |
| :---: | :---: |
| $100 \%$ ionized in aqueous solution | Partially ionized** in aqueous solution |
|  | hydrofluoric acid, HF |
| acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ |  |
| hydrochloric acid, HCl | nitrous acid, $\mathrm{HNO}_{2}$ |
| hydrobromic acid, HBr | hypochlorous acid, HOCl |
| hydroiodic acid, HI |  |
| perchloric acid, $\mathrm{HClO}_{4}$ | formic acid, $\mathrm{HCO} \mathrm{HCH}_{2} \mathrm{H}$ |
| nitric acid, $\mathrm{HNO}_{3}$ | hydrocyanic acid, HCN |
| sulfuric acid, $\mathrm{H}_{2} \mathrm{SO}_{4}$ | sulfurous acid, $\mathrm{H}_{2} \mathrm{SO}_{3}$ |
|  | carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$ |
| etc. |  |

**"Partially ionized" is not the same as "partially soluble." A weak acid can be very soluble in water, but only a small fraction of the acid molecules are ionized in aqueous solution.
14. Hydrofluoric acid, HF, is a weak acid that ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{HF}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{F}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \quad K_{a}=6.8 \times 10^{-4}
$$

(a) Write the expression for the equilibrium constant, $K_{a}$, for this reaction.

Compare your answer to part (a) with the $K_{a}$ expression on the AP Chemistry Equations and constants sheet.
(b) The pH of $0.50 \mathrm{MHF}(a q)$ is 1.74 .
(i) Calculate the value of $\left[\mathrm{H}^{+}\right]$in $0.50 \mathrm{MHF}(\mathrm{aq})$.
(ii) Calculate the percent ionization in $0.50 \mathrm{MHF}(\mathrm{aq})$.
15. Acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, is a weak acid found in household vinegar. Acetic acid ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \quad K_{a}=1.8 \times 10^{-5}
$$

(a) Do you predict that the pH of $0.50 M_{\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq}) \text { should be less than, greater than, or equal }}$ to the pH of $0.50 \mathrm{MHF}(a q)$ ? Your justification should include a comparison of the $K_{a}$ values for HF and $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and a comparison of the relative strength of these two acids.
(b) Fill in the missing information in the R-I-C-E table below. Let the variable " $x$ " represent the concentration of the hydronium ion at equilibrium.

| $\mathbf{R}$ eaction | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ | $\rightleftarrows$ | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ nitial | $\mathbf{0 . 5 0} \boldsymbol{M}$ |  | $\mathbf{N} / \mathbf{A}$ |  | $\mathbf{0} \boldsymbol{M}$ |  | $\approx \mathbf{0} \boldsymbol{M}$ |
| $\mathbf{C}$ hange |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |
| $\mathbf{E}$ quilibrium |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |

(c) Plug in all three values (in terms of $x$ ) from the bottom row of your R-I-C-E table into the $K_{a}$ expression shown below. Then solve for $x$.

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}=1.8 \times 10^{-5}
$$

On the AP Chemistry Exam, you will not need to use the quadratic equation to solve any mathematical calculations. Acetic acid is a weak acid. It is only partially ionized in aqueous solution. You can make the following assumption, in order to simplify the math in part (c).

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }} \text { is much smaller than }\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]_{\text {initial }}
$$

$$
(0.50 M-x) \approx 0.50 M
$$

(d) In part (c), you solved for $x$, which represents $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium in }} 0.50 M \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})$. Calculate the pH of $0.50 \mathrm{MHC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q)$.
16. Hypochlorous acid, HOCl , is a weak acid that forms when chlorine dissolves in water. HOCl molecules react with water molecules to form hypochlorite ions, $\mathrm{OCl}^{-}$, and hydronium ions.
(a) Write the balanced chemical equation for the ionization of HOCl in aqueous solution.
(b) Write the $K_{\mathrm{a}}$ expression for hypochlorous acid.
(c) The pH of $0.50 \mathrm{MHOCl}(a q)$ is 3.92 . Make a R-I-C-E table to help you calculate the concentrations of $\mathrm{HOCl}, \mathrm{H}_{3} \mathrm{O}^{+}$, and $\mathrm{OCl}^{-}$at equilibrium in $0.50 \mathrm{M} \mathrm{HOCl}(\mathrm{aq})$.
(d) Use the information from part (c) to calculate the value of $K_{a}$ for HOCl .

| Acid | HF | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | HOCl |
| :---: | :---: | :---: | :---: |
| Structural Formula | $\mathrm{H}-\underset{\mathrm{F}}{\square}$ : |  |  |
| $K_{a}$ | $6.8 \times 10^{-4}$ | $1.8 \times 10^{-5}$ | $2.9 \times 10^{-8}$ |
| $[\mathrm{HA}]_{\text {initial }}$ | 0.50 M | 0.50 M | 0.50 M |
| pH | 1.74 | 2.52 | 3.92 |
| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }}$ | 0.018 M | 0.0030 M | 0.00012 M |
| \% ionization | 3.6\% | 0.6\% | 0.024\% |

17. Use the information in the table above to answer the following questions.
(a) When comparing two different acids, the stronger acid is
the acid that has the ( lower higher ) $K_{\mathrm{a}}$ value.
(b) When comparing two different acids that have the same $[\mathrm{HA}]_{\text {initial }}$,
the stronger acid will have the ( lower higher ) pH .

There is an interesting relationship between $[\mathrm{HA}]_{\text {initial }}$ and the percent ionization of the acid.

|  | $[\mathrm{HA}]_{\text {initial }}$ | pH | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }}$ | Percent <br> Ionization |
| :---: | :---: | :---: | :---: | :---: |
| hydrofluoric acid | $1.0 M$ | 1.59 | $0.026 M$ | $2.6 \%$ |
|  | $0.50 M$ | 1.74 | $0.018 M$ | $3.6 \%$ |
|  | $0.10 M$ | 2.10 | $0.0079 M$ | $7.9 \%$ |
|  | $0.050 M$ | 2.26 | $0.0055 M$ | $11 \%$ |
|  | $0.010 M$ | 2.64 | $0.0023 M$ | $23 \%$ |


|  | $[\mathrm{HA}]_{\text {initial }}$ | pH | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }}$ | Percent <br> Ionization |
| :---: | :---: | :---: | :---: | :---: |
| acetic acid | $1.0 M$ | 2.38 | $0.0042 M$ | $0.42 \%$ |
|  | $0.50 M$ | 2.52 | $0.0030 M$ | $0.60 \%$ |
|  | $0.10 M$ | 2.89 | $0.0013 M$ | $1.3 \%$ |
|  | $0.050 M$ | 3.03 | $0.00094 M$ | $1.9 \%$ |
|  | $0.010 M$ | 3.38 | $0.00042 M$ | $4.2 \%$ |

18. As the value of $[\mathrm{HA}]_{\text {initial }}$ decreases...
...the value of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {equilibrium }}$ ( decreases increases ).
...the pH of the solution ( decreases increases ).
...the percent ionization of the acid ( decreases increases ).

The inverse relationship between $[\mathrm{HA}]_{\text {initial }}$ and the percent ionization of the acid can be explained in terms of Le Châtelier's principle.

$$
\mathrm{HA}(a q) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{A}^{-}(a q) \quad K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

During Unit 7, you learned the following.
If an aqueous equilibrium system is diluted with water, the concentrations of all aqueous species are decreased. As a result of this change, the aqueous equilibrium system shifts toward the side of the equation that has the higher number of moles of aqueous particles.

Suppose that 500 mL of $\mathrm{H}_{2} \mathrm{O}$ is added to 500 mL of a weak acid, HA.

$$
Q_{a}=\frac{\frac{1}{2}\left[\mathrm{H}^{+}\right] \frac{1}{2}\left[\mathrm{~A}^{-}\right]}{\frac{1}{2}[\mathrm{HA}]}=\frac{1}{2} K_{a}
$$

Dilution with water causes the value of $Q_{a}$ to become less than $K_{a}$. This causes a shift in the equilibrium with a net conversion from reactants to products. As a result, the percent ionization of the acid increases.

You have seen several examples of weak acids. Now let's examine the properties of weak bases.

| Strong Bases (Group I and II hydroxides) | Weak Bases |
| :---: | :---: |
| $100 \%$ dissociated into ions in aqueous solution | Partially ionized in aqueous solution |
| ammonia, $\mathrm{NH}_{3}$ |  |
| sodium hydroxide, NaOH | methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$ |
| potassium hydroxide, KOH | pyridine, $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ |
| calcium hydroxide, $\mathrm{Ca}(\mathrm{OH})_{2}$ | fluoride ion, $\mathrm{F}^{-}$ |
| strontium hydroxide, $\mathrm{Sr}(\mathrm{OH})_{2}$ | acetate ion, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$ |
|  | etc. |

19. Ammonia, $\mathrm{NH}_{3}$, is a weak base that ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q) \quad K_{b}=1.8 \times 10^{-5}
$$

(a) Write the expression for the equilibrium constant, $K_{b}$, for this reaction.

Compare your answer to part (a) with the $K_{b}$ expression on the AP Chemistry Equations and constants sheet.
(b) The pH of $0.50 \mathrm{MNH}_{3}(\mathrm{aq})$ is 11.48. Calculate the value of $\left[\mathrm{OH}^{-}\right]$in $0.50 M \mathrm{NH}_{3}(a q)$.
(c) Use the formula below and your answer to part (b) to calculate the percent ionization of the base in a solution of $0.50 \mathrm{M} \mathrm{H}_{3}(a q)$.

$$
\text { percent ionization }=\frac{\left[\mathrm{OH}^{-}\right]_{\text {equilibrium }}}{[\mathrm{B}]_{\text {initial }}} \times 100 \%
$$

Two important categories of weak bases are listed in the table below.

| neutral molecules co lone pair of electr | ing an atom with a at can accept $\mathrm{H}^{+}$ | anions that are the conjugate base of a weak acid |  |
| :---: | :---: | :---: | :---: |
|  <br> ammonia $\mathrm{NH}_{3}$ |  <br> methylamine $\mathrm{CH}_{3} \mathrm{NH}_{2}$ |  | $[: \ddot{\mathrm{Cl}}-\ddot{\mathrm{O}}:]^{-}$ <br> hypochlorite $\mathrm{ClO}^{-}$ |
|  <br> hydroxylamine $\mathrm{NH}_{2} \mathrm{OH}$ |  <br> pyridine $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ |  |  <br> hydrogen carbonate $\mathrm{HCO}_{3}{ }^{-}$ |

Acetic acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, and acetate, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$, represent a conjugate acid-base pair. The relationship between the values of $K_{a}$ and $K_{b}$ for a conjugate acid-base pair is represented by the equations below.

$$
K_{a} \times K_{b}=1.0 \times 10^{-14} \quad \text { at } 25^{\circ} \mathrm{C} \quad \mathrm{p} K_{a}+\mathrm{p} K_{b}=14.00 \quad \text { at } 25^{\circ} \mathrm{C}
$$

The example shown below is for the weak acid acetic acid $\left(\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)$ and its conjugate base acetate $\left(\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right)$. However, the relationship $K_{a} \times K_{b}=1.0 \times 10^{-14}$ works with any conjugate acid-base pair.

$$
\begin{aligned}
& \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(a q) \quad K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]} \\
& \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{OH}^{-}(a q)+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q) \quad K_{b}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]} \\
& \mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q) \quad K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=K_{a} \times K_{b}
\end{aligned}
$$

20. Propanoic acid, $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$, ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{2}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)
$$

(a) Write the expression for the equilibrium constant, $K_{a}$, for this reaction.
(b) The $\mathrm{p} K_{a}$ for $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$ is 4.88. Calculate the value of $K_{a}$ for $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$. $\qquad$
(c) Calculate the pH of $0.50 \mathrm{M} \mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}(a q)$.

The propanoate ion, $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{2}^{-}$, ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{2}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}(a q)+\mathrm{OH}^{-}(a q)
$$

(d) Calculate the value of $K_{b}$ for the propanoate ion, $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{2}{ }^{-}$. $\qquad$
(e) Calculate the pH of $0.50 \mathrm{M} \mathrm{NaC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}(\mathrm{aq})$.

