## Chapter 16

## Acid-Base Equilibria

## Arrhenius Definition

- Acids produce hydrogen ions in aqueous solution.
- Bases produce hydroxide ions when dissolved in water.
- Limits to aqueous solutions.
- Only one kind of base.
- $\mathrm{NH}_{3}$ ammonia could not be an Arrhenius base.


## Bronsted-Lowry Definitions

$\circ$ An acid is a proton $\left(\mathrm{H}^{+}\right)$donor and a base is a proton acceptor.

- Acids and bases always come in pairs.
-HCl is an acid.
- When it dissolves in water it gives its proton to water.
$\circ \mathrm{HCl}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Cl}^{-}$
- Water is a base makes hydronium ion


## Conjugate Pairs

- General equation
- $\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
- Acid + Base $\rightleftharpoons$ Conjugate acid +Conjugate base
- This is an equilibrium.
- Competition for $\mathrm{H}^{+}$between $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{A}^{-}$
- The stronger base controls direction.
- If $\mathrm{H}_{2} \mathrm{O}$ is a stronger base it takes the $\mathrm{H}^{+}$
- Equilibrium moves to right.



## Conjugate Pairs

$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})=\mathrm{NH}_{4}+(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
Label the Conjugate Pairs

- Water in the last example acted as a Bronsted-Lowry base, and here it is acting as an acid.
- AMPHIPROTIC or AMPHOTERIC


## Try One...

- What is the conjugate base of each of the following acids:
- $\mathrm{HClO}_{4}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{PH}_{4}{ }^{+1,} \mathrm{HCO}^{-1}$
- What is the conjugate acid of each of the following bases:
$\mathrm{CN}^{-}, \mathrm{SO}_{4}^{-2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{HCO}_{3}^{-1}$


## How about this one...

- The hydrogen sulfite ion is amphoteric.
- Write an equation for the reaction of this ion with water, in which the ion acts as an acid. Label the conjugate pairs.
- Write an equation for the reaction of this ion with water, in which the ion acts as a base. Label the conjugate pairs.


## A tricky one...

- When lithium oxide is dissolved in water, the solution turns basic from the reaction of the oxide ion with water.
- Write the reaction that occurs, and identify the conjugate acid-base pairs.


## Relative Strengths of Acids and Bases

- The stronger an acid, the weaker its conjugate base
- The stronger a base, the weaker its conjugate acid.

| Acid | Increasing acid strength | Base | Increasing base strength |
| :---: | :---: | :---: | :---: |
| $\mathrm{HCO}_{4}$ | 4 | $\mathrm{ClO}_{4}^{-}$ |  |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ |  | $\mathrm{HSO}_{4}{ }^{-}$ |  |
| HCl |  | $\mathrm{Cl}^{-}$ |  |
| $\mathrm{HNO}_{3}$ |  | $\mathrm{NO}_{3}^{-}$ |  |
| $\mathrm{H}_{3} \mathrm{O}^{+}$ |  | $\mathrm{H}_{2} \mathrm{O}$ |  |
| HF |  | $\mathrm{F}^{-}$ |  |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ |  | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$ |  |
| HOCl |  | $\mathrm{OCl}^{-}$ |  |
| $\mathrm{NH}_{4}{ }^{+}$ |  | $\mathrm{NH}_{3}$ |  |
| $\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{OH}^{-}$ |  |
| $\mathrm{NH}_{3}$ |  | $\mathrm{NH}_{2}{ }^{-}$ |  |
| $\mathrm{H}_{2}$ |  | $\mathrm{H}^{-}$ | $\checkmark$ |

## Acid, HA

\(\left.\begin{array}{ll}Stronger \& \mathrm{HClO}_{4} <br>
acid \& \left.\begin{array}{l}\mathrm{HCl}^{2} <br>
<br>
\mathrm{H}_{2} \mathrm{SO}_{4} <br>

\mathrm{HNO}_{3}\end{array}\right\}\end{array}\right\}\)| Strong acids. |
| :--- |
| $100 \%$ dissociated |
| in aqueous |
| solution. |

\(\left.$$
\begin{array}{l}\begin{array}{l}\mathrm{HSO}_{4}^{-} \\
\mathrm{H}_{3} \mathrm{PO}_{4} \\
\mathrm{HNO}\end{array}
$$ <br>
\mathrm{HF} <br>
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H} <br>
\mathrm{H}_{2} \mathrm{CO}_{3} <br>

\mathrm{H}_{2} \mathrm{~S}\end{array}\right\}\)|  |
| :--- |
|  |
| Weak acids. |
| Exist in solution |
| as a mixture of |
| $\mathrm{HA}, \mathrm{A}^{-}$, and $\mathrm{H}_{3} \mathrm{O}^{+}$. |

$\mathrm{NH}_{4}{ }^{+}$
HCN
$\mathrm{HCO}_{3}{ }^{-}$
$\mathrm{H}_{2} \mathrm{O}$

Weaker acid

Base, $\mathbf{A}^{-}$
$\mathrm{ClO}_{4}^{-}$
$\mathrm{Cl}^{-}$
$\mathrm{HSO}_{4}{ }^{-}$
$\mathrm{NO}_{3}{ }^{-}$
$\mathrm{H}_{2} \mathrm{O}$
$\left.\begin{array}{l}\mathrm{SO}_{4}{ }^{2-} \\ \mathrm{H}_{2} \mathrm{PO}_{4}^{-} \\ \mathrm{NO}_{2}^{-} \\ \mathrm{F}^{-} \\ \mathrm{CH}_{3} \mathrm{CO}_{2}^{-} \\ \mathrm{HCO}_{3}^{-} \\ \mathrm{HS}^{-}\end{array}\right\} \begin{aligned} & \\ & \\ & \text { Weak bases. } \\ & \text { Moderate tendency } \\ & \text { to be protonated in } \\ & \text { aqueous solution. }\end{aligned}$
 $\mathrm{H}^{-}$

## Strong Acids

- Completely transfer their protons to water
- Leaves no undissociated molecules in solution
- Their conjugate bases have a negligible tendency to be protonated in aqueous solutions.


## Weak acids

- Only partially dissociate in aqueous solution.
- Exist in the solution as a mixture of acid molecules and their constituent ions.
- Conjugate bases of weak acids show a slight ability to remove protons from water
- The conjugate bases of weak acids are weak bases.


## Negligible acidity

- Contain hydrogen but do not demonstrate any acidic behavior in water
- $\mathrm{CH}_{4}$, methane, for example
- Their conjugate bases are strong bases, reacting completely with water, abstracting protons to form OH - ions.


## Acid, HA

\(\left.\begin{array}{ll}Stronger \& \mathrm{HClO}_{4} <br>
acid \& \left.\begin{array}{l}\mathrm{HCl}^{2} <br>
<br>
\mathrm{H}_{2} \mathrm{SO}_{4} <br>

\mathrm{HNO}_{3}\end{array}\right\}\end{array}\right\}\)| Strong acids. |
| :--- |
| $100 \%$ dissociated |
| in aqueous |
| solution. |

\(\left.$$
\begin{array}{l}\begin{array}{l}\mathrm{HSO}_{4}^{-} \\
\mathrm{H}_{3} \mathrm{PO}_{4} \\
\mathrm{HNO}\end{array}
$$ <br>
\mathrm{HF} <br>
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H} <br>
\mathrm{H}_{2} \mathrm{CO}_{3} <br>

\mathrm{H}_{2} \mathrm{~S}\end{array}\right\}\)|  |
| :--- |
|  |
| Weak acids. |
| Exist in solution |
| as a mixture of |
| $\mathrm{HA}, \mathrm{A}^{-}$, and $\mathrm{H}_{3} \mathrm{O}^{+}$. |

$\mathrm{NH}_{4}{ }^{+}$
HCN
$\mathrm{HCO}_{3}{ }^{-}$
$\mathrm{H}_{2} \mathrm{O}$

Weaker acid

Base, $\mathbf{A}^{-}$
$\mathrm{ClO}_{4}^{-}$
$\mathrm{Cl}^{-}$
$\mathrm{HSO}_{4}{ }^{-}$
$\mathrm{NO}_{3}{ }^{-}$
$\mathrm{H}_{2} \mathrm{O}$
$\left.\begin{array}{l}\mathrm{SO}_{4}{ }^{2-} \\ \mathrm{H}_{2} \mathrm{PO}_{4}^{-} \\ \mathrm{NO}_{2}^{-} \\ \mathrm{F}^{-} \\ \mathrm{CH}_{3} \mathrm{CO}_{2}^{-} \\ \mathrm{HCO}_{3}^{-} \\ \mathrm{HS}^{-}\end{array}\right\} \begin{aligned} & \\ & \\ & \text { Weak bases. } \\ & \text { Moderate tendency } \\ & \text { to be protonated in } \\ & \text { aqueous solution. }\end{aligned}$
 $\mathrm{H}^{-}$

## Equilibrium Shifts

- In every acid-base reaction the position of the equilibrium favors transfer of the proton to the stronger base.
- The position of the equilibrium favors the reaction of the stronger acid and the stronger base to form the weaker acid and weaker base.
- As a result, the equilibrium mixture contains MORE of the weaker acid and weaker base and LESS of the stronger acid and stronger base.


## Practice...

- For the following proton-transfer reaction, use table 16.4 to predict whether the equilibrium lies predominantly to the left (that is Kc $<1$ ) or to the right ( $\mathrm{Kc}>1$ ):
$-\mathrm{HSO}_{4}^{-1}(\mathrm{aq})+\mathrm{CO}_{3}^{-2}(\mathrm{aq})=\mathrm{SO}_{4}^{-2}(\mathrm{aq})+$ $\mathrm{HCO}_{3}^{-1}$ (aq)


## Try These

- Use table 16.4 to predict whether the equilibrium lies predominantly to the left or to the right.
- $\mathrm{HPO}_{4}^{-2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})}=\mathrm{H}_{2} \mathrm{PO}_{4}^{-(\mathrm{aq})}+\mathrm{OH}^{-}(\mathrm{aq})$
- Aqueous ammonium ion reacts with aqueous hydroxide ion forming an equilibrium with aqueous ammonia and liquid water.


### 16.3 The Autoionization of Water

- Water autoionizes
- $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
- No individual molecule remains ionized for long
- Reactions are extremely rapid in both directions
- At room temp only about 2 out of every $10^{9}$ molecules are ionized at any given instant.


## The Ion Product of Water

- $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$
- At $25^{\circ} \mathrm{C} \mathrm{K} \mathrm{K}_{\mathrm{W}}=1.0 \times 10^{-14}$
- In EVERY aqueous solution.
- Neutral solution $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0$ $\times 10^{-7}$
- Acidic solution $\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]$
- Basic solution $\left[\mathrm{H}^{+}\right]<\left[\mathrm{OH}^{-}\right]$


## Practice Problems

- Calculate the values of [ $\mathrm{H}+$ ] and [OH-] ions in a neutral solution at 25 C.
- Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:
- $[\mathrm{H}+]=4 \mathrm{E}-9 \mathrm{M}$
- $[\mathrm{OH}-]=1 \mathrm{E}-7 \mathrm{M}$
- $[\mathrm{OH}-]=7 \mathrm{E}-13 \mathrm{M}$


## Another...

- Assume the problems occur at 25C.
- Calculate the concentration of the hydrogen ion in a solution in which the hydroxide ion concentration is 0.010 M .
- A solution in which the hydroxide ion concentration is $1.8 \mathrm{E}-9 \mathrm{M}$.


### 16.4 The pH Scale

- $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
- Used because $\left[\mathrm{H}^{+}\right]$is usually very small
- As pH decreases, $\left[\mathrm{H}^{+}\right]$increases exponentially
- Sig figs only the digits after the decimal place of a pH are significant
$\circ\left[\mathrm{H}^{+}\right]=1.0 \times 10^{-8} \mathrm{pH}=8.00 \quad 2$ sig figs
- $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$

| SUBST ANCES | pH |
| :---: | :---: |
| Hydrochloric Acid ( HCD | 0.0 |
| Giastrie Juices | 1.0 |
| Lemon duise | 2.3 |
| Vineqar | 2.9 |
| Wine | 3.5 |
| Tomato duice | 4.1 |
| Coffee (black) | 5.0 |
| Acid Rain | 5.6 |
| Urine | 6.0 |
| Rainwater | 6.5 |
| Milk: | 6.6 |
| Fiure 'water | 7.0 |
| Blood | 7.4 |
| Eaking Soda Solution | 8.4 |
| Eorax Solution | 9.2 |
| Toothpaste | 9.9 |
| Milk of Magnesia | 10.5 |
| Limewater | 11.0 |
| Household Ammonia | 11.9 |
| Sodium Hydroxide ( NaOH ) | 14.0 |

## Relationships

- $\mathrm{K}_{\mathrm{W}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$
$--\log K_{W}=-\log \left(\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]\right)$
$\circ-\log K_{W}=-\log \left[\mathrm{H}^{+}\right]+-\log \left[\mathrm{OH}^{-}\right]$
- $\mathrm{pK}_{\mathrm{w}}=\mathrm{pH}+\mathrm{pOH}$
- $K_{W}=1.0 \times 10^{-14}$
- $14.00=\mathrm{pH}+\mathrm{pOH}$
$\circ\left[\mathrm{H}^{+}\right],\left[\mathrm{OH}^{-}\right], \mathrm{pH}$ and pOH
Given any one of these we can find the other three.


## [ ${ }^{+}$]

## $10^{0} 10^{-1} 10^{3} 10^{-5} 10^{7} 10^{-9} 10^{-11} 10^{-13} 10^{-14}$ pH

Acidic
Neutral
Basic


## Practice Problems

- In a sample of lemon juice, the hydrogen ion concentration is 3.8 E -4 M . What is the pH ?
- A commonly available windowcleaning solution has a $[\mathrm{H}+$ ] of 5.3 $\mathrm{E}-9 \mathrm{M}$. What is its pH ?


## More Practice

- A sample of freshly pressed apple juice has a pH of 3.76. Calculate the [ $\mathrm{H}+$ ].
- Calculate the $[\mathrm{OH}-]$ and pOH as well.


## Measuring pH

- pH meter
- Digital readout
- Electrochemistry
- Acid-base indicators
- An organic molecule that is colored
- It exists in either an acid or base form (amphoteric) and each state is a different color).



## Strong Acids - 7 Memorize!

- Monoprotic
- $\mathrm{HBr}, \mathrm{HI}, \mathrm{HCl}, \mathrm{HNO}_{3}, \mathrm{HClO}_{4}, \mathrm{HClO} 3$
- Diprotic $=\mathrm{H}_{2} \mathrm{SO}_{4}$
- Completely dissociated - 100\%
- No equilibrium established, lies entirely to the right.
- To calculate pH of strong acids
- $\left[\mathrm{H}^{+}\right]=[\mathrm{HA}]$


## Try These...

- Calculating the pH of a strong acid

What is the pH of a 0.40 M solution of perchloric acid?

An aqueous solution of nitric acid has a pH of 2.34. What is the concentration of the acid?

## Strong Bases

- Relatively few strong bases.
- The $\mathrm{OH}^{-}$is a strong base.
- Hydroxides of the alkali metals are strong bases because they dissociate completely when dissolved.
- LiOH, RbOH, CsOH not commonly used in lab
- The hydroxides of the heavier alkaline earths $\mathrm{Ca}(\mathrm{OH})_{2}$ etc. are strong dibasic bases.
- Limited solubilities so they are used only when high solubility is not critical


## Other Strong Bases

- Strongly basic solutions are also created by certain substances that react with water to form hydroxide ions.
- Most common contain the oxide ion
- Metal oxides, especially Na 2 O and CaO , are often used in industry when a strong base is needed.
- $\mathrm{O}^{-2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow 2 \mathrm{OH}^{-}(\mathrm{aq})$


## Practice...

- A solution is formed by dissolving
0.0100 mol of sodium oxide in enough water to form 1.0 L solution.
- What is its [OH-] and pH ?


## More Examples

- Ionic hydrides and nitrides also react with water to form hydroxide.
- $\mathrm{H}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2}(\mathrm{~g})+\mathrm{OH}^{-}(\mathrm{aq})$
- $\mathrm{N}^{-3}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{NH}_{3}(\mathrm{aq})+3 \mathrm{OH}^{-}$ (aq)


## Calculate pH of strong base

- What is the pH of
- A 0.028 M solution of NaOH ?
- A 0.0011 M solution of calcium hydroxide?
- What is the concentration of a solution of
- KOH for which the $\mathrm{pH}=11.89$
- $\mathrm{Ca}(\mathrm{OH}) 2$ for which the pH is 11.68


### 16.6 Weak Acids

- Does not $100 \%$ dissociate in water
- Equilibrium is established
- $\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longleftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
- Or
- $\mathrm{HA}(\mathrm{aq})=\mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
- $\mathrm{Kc}=[\mathrm{H}+][\mathrm{A}-]=\mathrm{Ka}$
[HA]
- Acid-dissociation Constant
- Appendix D gives complete listings at 25C


## Magnitude of Ka

- The magnitude of Ka indicates the tendency of the acid to ionize in water
- The larger the value of Ka , the stronger the acid.
- It is favoring the products side of equilibrium.


## Calculating Ka from pH

- Ka will be small.
- ALWAYS WRITE THE MAJOR SPECIES.
- It will be an equilibrium problem from the start.
- Determine whether most of the $\mathrm{H}^{+}$will come from the acid or the water.
- Compare Ka or Kw


## Example

- A student prepared a 0.10 M solution of formic acid ( $\mathrm{HCHO}_{2}$ ) and measured its pH using a pH meter and found it to be 2.38 at 25 C .
- Calculate Ka for formic acid
- What percentage of the acid ionized in this 0.10 M solution?


## If Ka is quite small...

- It is okay to make some assumptions:
- Ka is small, equilibrium lies far to the left and that the initial concentration of the HA will be essentially the same number at equilibrium.
- Eliminates the need for the quadratic equation.
- When finding percent ionization to check assumption - a general rule is if the quantity of $x$ is more than $5 \%$ of the initial value, you had better use the quadratic formula.


## Another one...

- Niacin, one of the $B$ vitamins, has the following molecular structure:

- A 0.20 M solution of niacin has a pH of 3.26. What percentage of the acid is ionized in this solution. What is the Ka for niacin?


## Using Ka to calculate pH

- Step 1: Write the ionization equilibrium for the acid
- Step 2: Write the equilibriumconstant expression
- Step 3: Find the concentrations that are involved. Create an "ICE" Chart.
- Step 4: Substitute values into the equilibrium constant expression.


## Using Ka to calculate pH

- Calculate the pH of a 0.20 M solution of HCN. The value found in appendix $D$ is $4.9 \mathrm{E}-10$


## Using Ka to Calculate Percent Ionization

- Calculate the percentage of HF molecules ionized in a
- 0.10 M HF solution
- A 0.010 M HF solution
- By diluting the solution by a factor of 10, the percentage of molecules ionized increases by a factor of 3 .
- This is in accordance with LeChatelier's principle. There are more particles on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles because this counters the effect of the decreasing concentration of particles.


## More Practice

- Earlier, we found that the percent ionization of niacin ( $\mathrm{Ka}=1.5 \mathrm{E}-5$ ) in a 0.0200 M solution is $2.7 \%$.
Calculate the percentage of niacin molecules ionized in a solution that is
- 0.010 M
-1E-3 M


## Polyprotic acids

- Always dissociate stepwise.
- The first $\mathrm{H}^{+}$comes of much easier than the second.
- Ka for the first step is much bigger than Ka for the second.
- Denoted $\mathrm{Ka}_{1}, \mathrm{Ka}_{2}, \mathrm{Ka}_{3}$
- It is always easier to remove the first proton from a polyprotic acid than to remove the second., which is easier to remove than the third.
o Ka values become successively smaller


## Polyprotic acid

- $\mathrm{H}_{2} \mathrm{CO}_{3} \#+\mathrm{HCO}_{3}^{-}$

$$
\mathrm{Ka}_{1}=4.3 \times 10^{-7}
$$

$-\mathrm{HCO}_{3}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{CO}_{3}^{-2}$

$$
\mathrm{Ka}_{2}=4.3 \times 10^{-10}
$$

- Base in first step is acid in second.
- As long as the Ka values differ by a factor of $10^{3}$ or more, it is possible to obtain a satisfactory estimate of the pH of polyprotic acid solutions by considering only Ka1


## Example Problem

- The solubility of carbon dioxide in pure water at 25 C and 0.1 atm pressure is 0.0037 M . The common practice is to assume that all of the dissolved gas in the form of carbonic acid.
- What is the equation for this reaction?
- What is the pH of a 0.0037 M solution of carbonic acid? $\mathrm{Ka} 1=4.3 \mathrm{E}-7$ and $\mathrm{Ka} 2=$ 5.6 E-11
- What is the $\left[\mathrm{CO}_{3}^{-2}\right]$ ?


### 16.6 Weak Bases

- Many substances behave as weak bases in water.
- React with water abstracting protons
- $\mathrm{B}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})=\mathrm{HB}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
- Base dissociation constant, Kb
- $\mathrm{Kb}=\left[\mathrm{HB}^{+}\right]\left[\mathrm{OH}^{-}\right]$ [B]
Kb always refers to the equilibrium in which a base reacts with water to form the corresponding conjugate acid and OH -.


## Bases without $\mathrm{OH}^{-}$

- Bases are proton acceptors.
$-\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}$
$\circ$ It is the lone pair on nitrogen that accepts the proton.
- Many weak bases contain N
- Table 16.4, page 694


## Strength of Bases

- Hydroxides are strong.
- Others are weak.
- Smaller K ${ }_{\text {b }}$ weaker base.
- Example Problem: Calculate the pH of a solution of 4.0 M pyridine ( Kb $=1.7 \times 10^{-9}$ )



## Another Problem

- Calculate the concentration of hydroxide ion in a 0.15 M solution of ammonia.


## Using pH to Determine the Concentration of a Salt

- A solution made by adding solid sodium hypochlorite ( $\mathrm{NaClO} \mathrm{)} \mathrm{to} \mathrm{enough} \mathrm{water} \mathrm{to}$ make 2.0 L of solution has a pH of 10.50.
$\mathrm{ClO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{aq})=\mathrm{HClO}_{(\mathrm{aq})}+\mathrm{OH}^{-}(\mathrm{aq})$ $\mathrm{Kb}=3.3 \mathrm{E}-7$

Calculate the number of moles of sodium hypochlorite that were added to the water.

## Try this...

- A solution of ammonia in water has a pH of 11.17. What is the molarity of the solution?


### 16.8 Relationship between Ka and Kb

- Consider the conjugate acid-base pair of ammonia and ammonium ion. Each of these species reacts with water:
- $\mathrm{NH}_{4}{ }^{+}=\mathrm{NH}_{3}+\mathrm{H}^{+}$
- $\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O}=\mathrm{NH}_{4}+\mathrm{OH}^{-}$
- Express Ka for top equation
- Express Kb for bottom equation
- Add the two equations together


## Relationships

- $\mathrm{Ka} \times \mathrm{Kb}=\mathrm{Kw}=[\mathrm{H}+][\mathrm{OH}-]=$

$$
1 \mathrm{E}-14
$$

- pKa + pKb = pKw = 14

All at 25 C .

## Practice

- Using Appendix D, Calculate
- The Kb for the fluoride ion
- The Ka for the ammonium ion


### 16.9 Salts as acids an bases

- We need to examine the way that dissolved salts can affect pH .
- Salts are ionic compounds.
- We assume 100\% dissociation in water.
- Strong Electrolytes
- Many cations and anions are able to react with water to generate $\mathrm{H}+$ or OH - ions.
- This reaction is called HYDROLYSIS.


## Anions and Water

- $X$ - is considered a conjugate base of an acid.
- Cl - is the conj. base of HCl
- $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}-$ is the conj. base of $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
- If X - comes from a strong acid (one of the 7 we've memorized), it will not affect the pH of the solution.
- Conversely, if X-comes from a weak acid, it will abstract a proton from water, generating an OH - ion, and affect the pH .


## Take a look...

$\mathrm{X}-(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})=\mathrm{HX}(\mathrm{aq})+\mathrm{OH}-(\mathrm{aq})$
$\circ$ The hydroxide generated raises the pH , making it basic.
$-\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-}$

- Give it some thought...
- What effect will each of the following ions have on the pH of a solution:
- Nitrate and Carbonate?


## Cations and Water

- Polyatomic cations whose formulas contain one or more protons can be considered the conjugate acids of weak bases:
- $\mathrm{NH}_{4}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$
- Most metal ions can also react with water to decrease the pH. (Those from weak bases)
- Cations from strong bases DO NOT affect pH.
- This is Lewis Acid-Base Chemistry, coming up shortly.


## Give this some thought...

- Which of the following cations has no effect on the pH of a solution?
- Potassium ion
- Iron II ion
- Aluminum ion


## Combined Effect of Cation and Anion in Solution

1. An anion that is the conjugate base of a strong acid will not affect the pH .
2. An anion that is the conjugate base of a weak acid will cause the pH to increase.
3. A cation that is the conjugate acid of a weak base will cause the pH to decrease.

## Combined Effect of Cation and Anion in Solution

4. The cations of Group 1A and heavier members of group 2A (Ca+2, $\mathrm{Sr}^{+2}, \mathrm{Ba}^{+2}$ ) will not affect pH . These are the cations of the strong Arrhenius bases.
5. Other metal ions will cause a decrease in pH .

## Combined Effect of Cation and Anion in Solution

6. When a solution contains both the conjugate base of a weak acid and conjugate acid of a weak base, the ion with the larger equilibrium constant Ka or Kb will have the greater influence on the pH .

- $\mathrm{K}_{\mathrm{a}}>\mathrm{K}_{\mathrm{b}}$ acidic
- $\mathrm{K}_{\mathrm{a}}<\mathrm{K}_{\mathrm{b}}$ basic
- $\mathrm{K}_{\mathrm{a}}=\mathrm{K}_{\mathrm{b}} \quad$ Neutral


## Sample Problem

- List the following solutions in order of increasing pH
- 0.1 M Barium acetate
- 0.1 M ammonium chloride
- 0.1 M Methyl amine bromide ( $\mathrm{NH}_{3} \mathrm{CH}_{3} \mathrm{Br}$ )
- 0.1 M potassium nitrate


## Try this...

- In each of the following, indicate which salt will form the more acidic 0.01 M solution.
- Sodium nitrate or iron (III) nitrate
- Potassium bromide or potassium hypobromite
- Methyl amine chloride or barium chloride
- Ammonium nitrite or ammonium nitrate


## Still more practice...

- Predict whether the salt, sodium hydrogen phosphate, will form an acidic solution or a basic solution when dissolving in water. (It is amphoteric)


### 16.10 Acid-Base Behavior and Chemical Structure

## Factors that Affect Acid Strength

1. The polarity of the $\mathrm{H}-\mathrm{X}$ Bond

- $\mathrm{H}--->X$ and not the reverse ( NaH )
- Nonpolar HX bonds produce neither acid nor basic solutions. ( CH 4 )

2. The strength of the $\mathrm{H}-\mathrm{X}$ Bond

- Stronger bonds are less easily dissociated than weaker ones.
- HF is too strong a bond and therefore a weak acid while all other hydrogen halides are strong acids.

3. The stability of the conj. base, X-

- The greater the stability of the conj base, the stronger the acid.


## Binary Acids

- The $\mathrm{H}-\mathrm{X}$ bond strength is the most important factor determining acid strength among the binary acids, $H X$, where $X$ - is in the same GROUP.
- Strength of bond decreases as the element X increases in size.
- Example, HCl stronger than HF
- $\mathrm{H}_{2} \mathrm{~S}$ stronger than $\mathrm{H}_{2} \mathrm{O}$


## Binary Acids

- Bond polarity is the major factor determining the acidity for binary acids in the same period.
- Acidity increases as the
electronegativity of the element X increases
- Left to right in a row
- $\mathrm{CH} 4 \ll \mathrm{NH}_{3} \ll \mathrm{H}_{2} \mathrm{O} \ll \mathrm{HF}$


## Strength of oxyacids

- The more oxygen hooked to the central atom, the more acidic the hydrogen.
- $\mathrm{HClO}_{4}>\mathrm{HClO}_{3}>\mathrm{HClO}_{2}>\mathrm{HClO}$
- Remember that the H is attached to an oxygen atom.
- The oxygens are electronegative
- Pull electrons away from hydrogen
- Another way to say it... in a series of oxyacids, the acidity increases as the oxidation number of the central atom increases.


## Strength of oxyacids



$$
\mathrm{Cl}-\mathrm{O}-\mathrm{H}
$$

## Strength of oxyacids



$$
\mathrm{O}-\mathrm{Cl}-\mathrm{O}-\mathrm{H}
$$

## Strength of oxyacids



## Strength of oxyacids



## Practice Problem

- Arrange the compounds in each of the following series in order of increasing acid strength:
- $\mathrm{AsH} 3, \mathrm{HI}, \mathrm{NaH}, \mathrm{H}_{2} \mathrm{O}$
- $\mathrm{H}_{2} \mathrm{SeO}_{3}, \mathrm{H}_{2} \mathrm{SeO}_{4}, \mathrm{H}_{2} \mathrm{O}$


## Try this...

- In each of the following pairs choose the compound that leads to the more acidic solution
- HBr, HF
- $\mathrm{PH}_{3}, \mathrm{H}_{2} \mathrm{~S}$
- $\mathrm{HNO}_{2}, \mathrm{HNO}_{3}$
- $\mathrm{H}_{2} \mathrm{SO}_{3}, \mathrm{H}_{2} \mathrm{SeO}_{3}$


## Carboxylic Acids (Organic Acids)

-     - COOH is the carboxyl group
- Acetic Acid, $\mathrm{CH}_{3} \mathrm{COOH}$
- Formic Acid, HCOOH
- Benzoic Acid, $\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{COOH}$
- The acid strength of carboxylic acid also increases as the number of electronegative atoms in the acid increases.
- $\mathrm{CF}_{3} \mathrm{COOH}$ is much more acidic than $\mathrm{CH}_{3} \mathrm{COOH}$


### 16.11 Lewis Acids and Bases

- Most general definition.
- Acids are electron pair acceptors.
$\bigcirc$ Bases are electron pair donors.



## Lewis Acids and Bases

## - Boron triflouride wants more electrons.



## Lewis Acids and Bases

$-\mathrm{BF}_{3}$ is Lewis Acid
$\circ \mathrm{NH}_{3}$ is a Lewis Base.


## Acid-Base Properties of Oxides

- Non-metal oxides dissolved in water can make acids.
$-\mathrm{SO}_{3}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longrightarrow \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$
- Water acts as electron pair donor
- $\mathrm{SO}_{3}$ acts as electron pair receptor
$\circ \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$


## Hydrolysis of Metal Ions

- Highly charged metal ions pull the electrons of surrounding water molecules toward them.

- Make it easier
for $\mathrm{H}^{+}$to come off.


## Lewis Acids and Bases

$$
\begin{aligned}
& \mathrm{Al}^{+3}+6\left(\ddot{:}_{\mathrm{H}}^{\prime \mathrm{H}}\right) \\
& \left.\mathrm{Al}-\left(\ddot{\mathrm{O}}_{\mathrm{H}}^{\mathrm{H}}\right)_{6}\right]^{+3}
\end{aligned}
$$

## Hydration

- When metal ions attract the unshared electron pairs of water molecules.
- Can be thought of as a Lewis acid-base interaction.
- Hydrolysis reactions generally increase with increasing charge and decreasing radius of the ion.
- $\mathrm{Cu}^{+2}$ has a smaller charge and larger radius than $\mathrm{Fe}^{+3}$, therefore forms less acidic solutions.


## Give it some thought...

- Which of the following cations will be most acidic and why?
- $\mathrm{Ca}^{2+}, \mathrm{Fe}^{2+}, \mathrm{Fe}^{3+}$


## Putting it all together...

- Phosphorous Acid has the following Lewis Structure:
- Explain why phosphorous acid is diprotic and not triprotic.
- A 25.0 mL sample of solution of the acid is titrated with 0.102 M NaOH , It required 23.3 mL of NaOH to neutralize both acidic protons. What is the molarity of the acid solution?
- This solution has a pH of 1.59. Calculate the percent ionization and Ka1 for the acid, assuming that Ka1>>Ka2.
- How does the osmotic pressure of a 0.50 M solution of HCl compare with that of a 0.50 M solution of the acid? Explain.

