**Important Topics in Acid-Base Chemistry**

**Acid/Base Concepts and Definitions**

**Arrehenius:** an acid increases the concentration of $\text{H}^+([\text{H}^+])$ in an aqueous ($\text{aq}$) solution.

Note: $[\text{H}^+] = [\text{H}_3\text{O}^+]$, i.e. the conc. of $\text{H}^+$ is the same as the conc. of $\text{H}_3\text{O}^+$ in an aqueous solution.

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

A base increases the concentration of $\text{OH}^-$ ($[\text{OH}^-]$) in an aqueous solution.

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

A strong acid completely ionizes (dissociates into ions), i.e. 1 mole of HCl completely ionizes forming 1 mole of $\text{H}_3\text{O}^+$ and 1 mole of $\text{Cl}^-$.

A strong base completely ionizes (dissociates into ions), i.e. 1 mole of $\text{Ba(OH)}_2$ completely ionizes forming 2 mole of $\text{OH}^-$ and 1 mole of $\text{Ba}^{2+}$.

A weak acid does not completely ionize which means that an equilibrium exists between the un-ionized acid and the ionized acid.

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

A weak base does not completely ionize which means that an equilibrium exists between the un-ionized base and the ionized base.

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

**Brønsted-Lowry:** an acid donates a proton, $\text{H}^+$, in a proton transfer reaction.

A base accepts a proton, $\text{H}^+$, in a proton transfer reaction.

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

**Lewis:** an acid accepts an electron pair when forming a covalent bond (a vacant orbital is available).

A base donates an electron pair when forming a covalent bond.

$$\text{F}_3\text{B(g) + :NH}_3(g) \rightarrow \text{F}_3\text{B-NH}_3$$

$$\text{Co}^{2+}(aq) + \text{H}_2\text{O(l)} \rightarrow [\text{Co-OH}_2]^3+(aq)$$

$$\text{H}^+(aq) + :\text{NH}_3(aq) \rightarrow \text{H-NH}_3^+(aq) (\text{NH}_4^+, \text{ammonium})$$
How does one determine the favored direction of a Brønsted-Lowry acid-base reaction?

1) Identify the acid-base conjugate pairs.
2) Identify the weakest conjugate base of each pair. Use Table 17.1 on page 671 in Petrucci. **Weakest means Most Stable**
3) Choose the direction that forms the weakest conjugate base.

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

1) A1  B2  A2  B1

2) B2 is weaker than B1 according to Table 17.1
3) The favored direction is toward reactants, A1 and B2

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

Ionization Equilibria for Weak Acids and Bases

Acid: \( \text{H}_2\text{S(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HS}^-(aq) + \text{H}_3\text{O}^+(aq) \)

\[ K_c = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}][\text{H}_2\text{O}]} \]

\[ K_a = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} \]

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

\[ K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \]

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

See Table 17.3, page 678 for \( K_a \) and \( K_b \) values for a number of weak acids and bases.

Degree of Ionization (x 100 = Percent Ionization): The fraction of molecules (weak acid or base) that react with water to give ions. If acid HA has a degree of ionization of 0.10 (10.%) then for every 10 HA molecules, only 1 molecule ionizes in water to \( \text{H}_3\text{O}^+ \) and \( \text{A}^- \). Percent Ionization increases as a solution of a weak acid or base is diluted. Why?

Polyprotic Acids

"many protons": \( \text{H}_2\text{CO}_3^-(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \) \( K_{a1} = 4.3 \times 10^{-7} \)

\( \text{HCO}_3^-(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \) \( K_{a2} = 4.8 \times 10^{-11} \)

\( K_{a2} < K_{a1} \) Generally, subsequent ionizations are less favored. Why?

Autoionization of Water, An Equilibrium

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

\[ K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \]

\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \]

Note the magnitude of \( K_w \), what does it mean? \( K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \) at 25 °C, pure water

In pure water, \([\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}\)

A solution is **acidic** if \([\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \), **neutral** if \([\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \), and **basic** if \([\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \)
pH: “potential of hydrogen ion” (Apparently devised by a Dane named Sørensen while brewing beer)

\[ \text{pH} = -\log[H^+] \]

Note, we are considering the pH of only aqueous solutions, so \([H^+] = [H_3O^+]\). Remember too that \([H^+]\) really means the activity of \(H^+ ([H^+]/[1 \text{ M}])\) which is unitless, thus pH is unitless.

An aqueous solution has \([H^+] = 2.56 \times 10^{-4} \text{ M}\), \(\text{pH} = -\log(2.56 \times 10^{-4}) = 3.592\)

The number of significant digits in the concentration = the number of decimal places in the mantissa

\(3 = \text{characteristic, .592 = mantissa}\)

pH in aqueous solution ranges from 0-14. \(\text{pH + pOH = 14.00}\)

A solution is **acidic** if pH < 7, **neutral** if pH = 7, and **basic** if pH > 7

**Problem Solving Techniques**: See pages 679-681 and pages 683-684

(pages 688-689 discuss general techniques that we may cover)

**Acid-Base Properties of Salt Solutions**

Salts may be obtained by neutralizing an acid with a base in aqueous solution. Given this neutralization, the aqueous salt solution that is produced is generally considered neutral in terms of pH. However, this is only true when a strong acid is neutralized with a strong base (\(\text{HCl + NaOH = NaCl + H}_2\text{O}\)).

Consider an aqueous solution of NaCN: \(\text{NaCN(s) } -\rightarrow \text{Na}^+(aq) + \text{CN}^-(aq)\)

The pH of a 0.1 M solution of NaCN has a pH = 11.1. How can this solution be basic?

The cyanide ion, \(\text{CN}^-\), unlike \(\text{Na}^+\), reacts with water: \(\text{CN}^-(aq) + \text{H}_2\text{O(l)} \stackrel{\text{\equiv}}{\rightarrow} \text{HCN(aq) + OH}^-(aq)\)

Notice what happens here, the cyanide ion accepts a proton from water to form its conjugate acid, HCN, and hydroxide, the strongest base that exists in water. It is this presence of hydroxide that makes the salt solution basic.

The term for an ion that reacts with water to generate the conjugate acid and hydroxide (see example above) or the conjugate base and hydronium (see example below) is **hydrolysis**.

Consider an aqueous solution of \(\text{NH}_4\text{Cl}\): \(\text{NH}_4\text{Cl(s) } -\rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)\)

\(\text{NH}_4^+(aq) + \text{H}_2\text{O(l)} \stackrel{\text{\equiv}}{\rightarrow} \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)\) This hydrolysis makes the salt solution acidic.

**General Rules**

If a salt can be made from a strong acid and strong base, no hydrolysis occurs in the salt solution-neutral.

If a salt can be made from a strong acid and weak base, hydrolysis occurs to give an acidic salt solution.

If a salt can be made from a weak acid and strong base, hydrolysis occurs to give a basic salt solution.

If a salt can be made from a weak acid and weak base, both ions of the salt hydrolyze. The salt solution is acidic if \(K_a\) of the cation is greater than \(K_b\) of the anion.

**Clever Relationships**

\[ K_a (\text{acid}) \times K_b (\text{its conjugate base}) = K_w \]

\[ [\text{HS}^-][\text{H}_3\text{O}^+]/[\text{H}_2\text{S}] \times [\text{H}_2\text{S}][\text{OH}^-]/[\text{HS}^-] = [\text{H}_3\text{O}^+][\text{OH}^-] \]

\[ K_b (\text{base}) \times K_a (\text{its conjugate acid}) = K_w \]

\[ [\text{HCN}][\text{OH}^-]/[\text{CN}^-] \times [\text{CN}^-][\text{H}_3\text{O}^+]/[\text{HCN}] = [\text{OH}^-][\text{H}_3\text{O}^+] \]
**Trends in Acidity, Basicity, and Stability**

Ordered from least acidic to most acidic: \( HF < HCl < HBr < HI \)  
Why?

The most acidic acid will have the most stable (weakest) conjugate base
Ordered from least stable to most stable: \( F^- < Cl^- < Br^- < I^- \)  
Why?

Charged species are unstable relative to uncharged species. Giving a neutral species a charge requires energy to be added. The species that can distribute the charge within the largest volume is most stable. \( I^- \) has the largest volume, hence it is most stable and its conjugate acid, HI, is most acidic.

The trend here is that as you go down a column of elements their binary acids, HA, increase in acidity. It should also be noted that the H-A bond decreases in strength in going down a column of elements.

Can you explain the following acidity trend \( CH_4 < NH_3 < H_2O < HF \)? Realize that you are going across a row of elements making up HA?

Strengths of oxoacids: \( HOCl > HOBr \). Why? Consider the relative stabilities of the conjugate bases.

\( H_2SO_4 \) is a stronger acid than \( H_2SO_3 \) \( (K_{a1}: 10^3 > 1.3 \times 10^{-2}) \). Why is this? Your text talks about a greater electron withdrawing ability for \( H_2SO_4 \) as a reason behind its relative acid strength. Well that’s true enough, but think about the effect of the oxidation state of the sulfur in combination with this reason.

The effect of resonance for the stabilization of an acid’s conjugate base-acetic acid vs. methanol, p. 695.

The effect of induction for the stabilization of an acid’s conjugate base-chloroacetic acid vs. acetic acid, p.696.