Acid- Base Equilibrium

AP Chemistry 30 – Ms. Hayduk

Acid-Base Theories

Arrhenius

- Acids contain hydrogen
  - Donate hydrogen ion in water
  - e.g. HCl (g) → H^+ (aq) + Cl^- (aq)
- Bases contain hydroxide
  - Donate hydroxide ion in water
  - e.g. KOH (s) → K^+ (aq) + OH^- (aq)

Acid-Base Theories

- Arrhenius is limited – what about bases without OH^-? ($NaHCO_3$, NH_3…)

Bronsted-Lowry

- Acids donate a proton in water
  - e.g. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$
- Bases accept a proton in water
  - e.g. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Hydrogen vs. Hydronium

- Hydronium is H_3O^+ - basically a hydrogen ion attached to a water molecule
- EQUIVALENT – think "Robert" vs. "Bob" (same guy, just one name is shorter)

Conjugates

- Conjugate acid-base pair: compounds that differ by one hydrogen ion
- Example:

HNO_3 +	H_2O →	H_3O^+ +	NO_3^-
Acid	Base	Conjugate Acid	Conjugate Base

Example: Conjugates

Identify the conjugate acid-base pairs.

H_2O (l) + NH_3 (aq) ⇌ NH_4^+ (aq) + OH^- (aq)

HF (aq) + H_2O (l) ⇌ F^- (aq) + H_3O^+ (aq)

Worth Noting…

- Acids often, but not always, start with H – they must contain hydrogen to be a B-L acid
- Acids can be cations, anions or neutral
- Bases can be anions or neutral

Thinking Activity

a. Identify the acid, base, conjugate acid and conjugate base:

$$HBr + NH_3 \rightarrow NH_4^+ + Br^-$$

b. What is the conjugate base of H_2S?

c. What is the conjugate acid of NO_3^-?

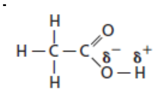
d. How can you tell if two compounds are a conjugate acid-base pair?

Amphoteric Substances

- **Amphiprotic**: substances that can donate or accept a hydrogen ion
- **Amphoteric**: substances that can act as either an acid or a base
- All amphiprotic substances are amphoteric, but the reverse is not true
- Example: water, HCO_3^-

Ionization of Acids

- Only available hydrogen ions to lose are from <u>polar bonds</u>.
- Process is called ionization – breaking a polar bond to form two ions
- For example, in acetic acid:



Three H-C bonds will not be broken in water, but O-H can be

Available Hydrogen

- **Monoprotic** acids: one available H^+
  - e.g. HF, $HClO_4$, $HC_2H_3O_2$
- **Diprotic** acids: two available H^+
  - e.g. $H_2C_2O_4$
- **Polyprotic** acids: many available H^+
  - e.g. H_3PO_4
- **Polyprotic bases**: accept more than one H^+ (anions with -2 and -3 charges)

Successive Ionization

- Acids donate only one proton at a time
- Each ionization is more difficult

Strength of Acids and Bases

- **Strength** of an acid or base: extent to which it dissolves in solution
- Basically, strength is an indicator of how soluble the compound is

Strong Acids

- Dissolve **100%** in solution (very soluble)
- All of the non-water particles are **ions**
- Six strong acids – YOU MUST MEMORIZE THESE
  - Hydrohalic acids HCl, HI, HBr (NOT HF)
  - Nitric acid HNO_3
  - Sulfuric acid H_2SO_4
  - Perchloric acid $HClO_4$

Strong Acids

- Affected by bond strength (lower bond strength = stronger acid, because it breaks apart more easily)

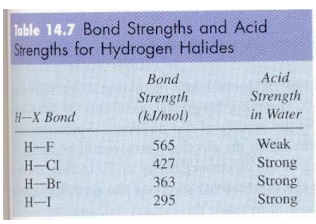
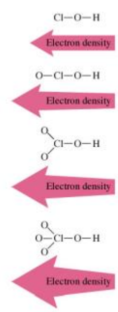


Table 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Strong Acids

- More oxygen within an oxyacid means the acid is stronger
- $HClO_4$ is very strong, $HClO_3$ is somewhat strong, and $HClO_2$ and HClO are weak

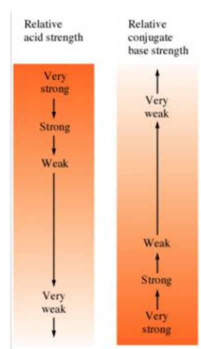


Strong Bases

- YOU MUST MEMORIZE:
  - Hydroxides and oxides of IA and IIA metals, EXCEPT Mg and Be
- Strong acids/bases have **highly polar bonds** –easily broken apart by water

Strength and Conjugates

- Strong acids and bases have very weak conjugates (no reverse reaction)
- Converse is also true



Weak Acids and Bases

- Ionize very little in solution
- Equilibrium between the compound (as a neutral molecule) and its ions
- Almost non-polar bonds (do not dissolve easily in water)
- Temperature and concentration can also affect the level of dissociation of any substance being dissolved in water

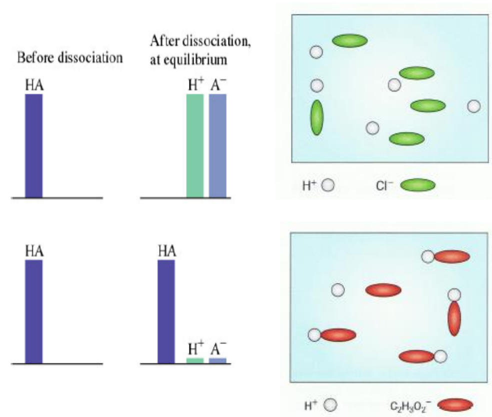


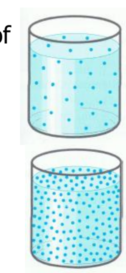
Table 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

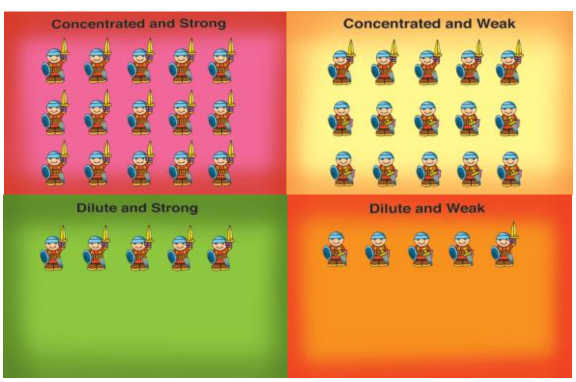
Concentration Versus Strength

A **dilute** solution has a small amount of acid or base particles (either ions or molecules) per unit volume of solution.

A **concentrated** solution has a large amount of acid or base particles per unit volume.



The strength of an acid or base does not affect its ability to be concentrated or dilute.



Acid Ionization Equations

- Strong acids **ionize** completely:

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

- Weak acids ionize partially, so they are in equilibrium:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- Can write these without H_2O (produce H^+)

Example: Ionization Equations

Write a balanced equation for the ionization of hydrochloric acid:

Write the balance equation for the first ionization of carbonic acid, H_2CO_3:

Base Dissociation/Ionization Equations

- Strong bases dissociate completely:

$$BOH \rightarrow B^+ + OH^-$$

- Weak bases ionize partially, so they are in equilibrium. A weak base MUST be combined with **water**, to produce hydroxide ions:

$$B + H_2O \rightleftharpoons OH^- + HB$$

Example: Ionization/Dissociation Equations

Write a balanced equation for the dissociation of sodium hydroxide:

Write a balanced equation for the ionization of methylamine, CH_3NH_2:

Ionization Constants

- K_a and K_b are acid and base **ionization constants**
- Similar to K_{sp} – determine how much an acid/base will ionize in solution
- Higher values mean the acid or base is stronger
- Compare strength using these values

Example: K_a

Put these in order from strongest to weakest:

Formic acid	1.8×10^{-4}
Hydrocyanic acid	6.2×10^{-10}
Citric acid	3.2×10^{-7}
Boric acid	5.9×10^{-10}
Benzoic acid	6.4×10^{-5}

Ionization Constants

- K_a and K_b have equilibrium expressions
- For example, for acetic acid:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

- For polyprotic acids, there is a constant for each successive ionization

Example 1: Strong Acids

Calculate $[H^+]$ in a 2.00 M solution of hydrochloric acid. K_a for HCl is very large.

Example 2: Strong Bases

Calculate $[OH^-]$ in a 1.50 M solution of calcium hydroxide, a strong base.

Example 3: Weak Acids

An acetic acid ($HC_2H_3O_2$) solution is 0.25 mol/L. Given that K_a for acetic acid is 1.8×10^{-5}, find $[H^+]$.

Example 4: K_b for Weak Bases

Calculate the hydroxide ion concentration in a 0.025 M solution of aniline, $C_6H_5NH_2$, a weak base with $K_b = 4.3 \times 10^{-10}$.

Water

- Water ionizes very slightly to produce equal hydronium and hydroxide ions

  $H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$

- Autoionization constant of water, K_w at 25°C is given by:

  $$K_w = [H_3O^+][OH^-] = 1.008 \times 10^{-14}$$

  $K_w = K_a \times K_b$ for a conjugate pair

Acidity and Basicity

- If $[OH^-] = [H^+]$, solution is neutral
- If $[OH^-] > [H^+]$, solution is basic
- If $[OH^-] < [H^+]$, solution is acidic

Thinking Activity

At 60°C, K_w is 1.0×10^{-13}.

Using Le Chatelier's Principle, determine whether the ionization of water is exothermic or endothermic.

$$2\ H_2O\ (l) \leftrightharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

Example: K_w

In a solution, $[H^+] = 3.82 \times 10^{-11}$ M. What is $[OH^-]$ in the solution? Is the solution neutral, basic or acidic?

pH and pOH

- Use pH to simplify concentration values (often very small numbers)
- Logarithmic scale that indicates the concentration of ions in a solution:

$$pH = -\log [H^+]$$
$$pOH = -\log [OH^-]$$
$$pH + pOH = 14.00$$

pH and pOH

- pH Ranges:
  - Acids pH < 7
  - Neutral pH = 7
  - Bases pH > 7
- It is a myth that pH must fall between 0 and 14 – can be outside of that range for concentrated acids and bases

Notes about Logs

- For a log scale, each integer represents a magnitude of 10
  - A solution with pH of 3 is ten times more acidic than a solution with pH 4
  - A solution with pH 3 is a hundred times more than pH 5
- Significant digits with logs – write as many decimal places on pH as there are in the least accurate measurement you are given

pH to Concentration

To calculate the concentration from pH or pOH:

$$[H^+] = 10^{-pH}$$
$$[OH^-] = 10^{-pOH}$$

Example 1: pH

A solution at 25°C has a pH of 8.22. Calculate pOH, $[H^+]$ and $[OH^-]$ for the solution.

Example 2: pH

For a 0.15 mol/L solution of hydrobromic acid, what is the pH of the solution?

Example 3: pH

What is the pH of a 2.6×10^{-5} M barium hydroxide solution?

pH of Weak Acid Solutions

- To solve:
  - Balanced equation
  - K_a expression
  - ICE table
  - Solve for *x*

Example 1: pH of a Weak Acid

Calculate the pH of a 1.00×10^{-6} M solution of acetic acid, $HC_2H_3O_2$. The K_a of acetic acid is 1.8×10^{-5}.

Neglecting *x*

- Sometimes the $-x$ in the denominator can be considered negligible
- Look at the original concentration and compare it to $100K_a$ (or $100K_b$)
  - If the initial concentration is larger than $100K_a$, then the *x* in the denominator is negligible
- In the previous example, $100K_a$ is too close to the initial C to neglect $-x$

Example 2: pH of a Weak Acid

Calculate the pH of a 1.10 M solution of acetic acid, $HC_2H_3O_2$. The K_a of acetic acid is 1.8×10^{-5}.

Weak Acid Mixtures

- Only the acid with the largest K_a will contribute a significant amount of H^+
- Determine the pH based on this acid and ignore any other

Example: Weak Acid Mixtures

Calculate the pH of a solution that contains 2.55 M HCN ($K_a = 6.2 \times 10^{-10}$) and 1.33 M HNO_2 ($K_a = 4.0\times 10^{-4}$). Also, determine the concentration of the cyanide ion (CN^-) in this solution at equilibrium.

Percent Ionization

- How ionized the weak acid or base is
- Given by:

$$\% = \frac{[x]}{[C]_o} \times 100$$

Where x is $[H_3O^+]$ or $[OH^-]$

Example 1: Percent Ionization

Calculate the percent ionization of acetic acid ($K_a = 1.8 \times 10^{-5}$) in a 0.500 M solution.

Example 2: Percent Ionization

In a 0.125 M aqueous solution of nitrous acid (HNO_2), 6.5% is ionized. Calculate K_a for this acid.

pH of Weak Bases

- Remember:
  - Ionization equation must include H_2O
  - The value for *x* will be $[OH^-]$, and the negative log will give you pOH

Example: pH of Weak Bases

For a 0.00675 mol/L solution of aniline, $C_6H_5NH_2$, K_b is 4.2×10^{-10}. What is the pH of the solution?

pH for Polyprotic Acids

- Remember: ionization will occur in steps
- First ionization will be the greatest, and subsequent will produce fewer and fewer hydrogen ions (more difficult to remove the proton)
- EXCEPT sulfuric acid, 2nd and 3rd ionization can be considered negligible

Example: pH of a Polyprotic Acid

Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}.

Formula	K_{a_1}	K_{a_2}	K_{a_3}
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}

Sulfuric Acid

- Special case, since first ionization is strong
- For concentrations over 1.0 M, ignore the second ionization
- If the concentration is less than 1.0 M, then the second ionization is not negligible (need a quadratic to solve)

Acid-Base Properties of Salts

- Salts are produced during acid-base reactions
- Not always neutral – some will react with water to produce acidic or basic solutions

Neutral Salts

- Produced from a strong acid reacted with a strong base
- Example: $NaNO_3$
  - Which acid and base reacted to produce this salt?
  - $NaOH$ (strong base) and HNO_3 (strong acid)

Basic Salts

- Formed from the cation of a strong base and the anion of a weak acid
- Anion will react (hydrolyze) with water to produce a weak acid and OH^- (strong base)
- Example: $KC_2H_3O_2$ ($KOH + HC_2H_3O_2$)
  - $C_2H_3O_2^- + H_2O \leftrightharpoons OH^- + HC_2H_3O_2$

Acidic Salts

- Formed from the cation of a weak base and the anion of a strong acid
- Cation will react (hydrolyze) with water to produce a weak base and H_3O^+ (strong acid)
- Example: NH_4Cl ($NH_3 + HCl$)
  - $NH_4^+ + H_2O \leftrightharpoons NH_3 + H_3O^+$

Weak Acids + Weak Bases

- If a weak acid and weak base are combined, determine which has a larger K value (K_a or K_b)
- The value that is higher determines the pH of the salt solution

Table 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Steps to Solve

1. Which acid and base reacted to form the salt?
2. Are those acids strong or weak?
3. Strong wins
   - strong acid = acidic salt, write $\leftrightharpoons H_3O^+$
   - strong base = basic salt, write $\leftrightharpoons OH^-$
4. Strong is a spectator – use remaining ion of salt with water as reactants
5. Other product is original weak acid/base

Example 1: pH of Salts

What is the qualitative pH of $Fe(NO_3)_3$?

1. Which acid reacted? Strong or weak?
2. Which base reacted? Strong or weak?
3. Which "wins"? Write $H_2O \leftrightharpoons$ ____
4. Add "weak" ion and original weak acid/base

Thinking Activity

Determine whether the following salts will form acidic, basic or neutral solutions.

Example 2: pH of Salts

Calculate the pH of a 0.30 M NaF solution. K_a for HF is 7.2×10^{-4}.

Example 3: pH of Salts

Calculate the pH of a 0.10 M NH_4Cl solution. K_b for NH_3 is 1.8×10^{-5}.