

ACIDS AND BASES

DEFINITIONS:

Arrhenius Definition

An **acid** in aqueous solution produces H^+ ions.

A **base** in aqueous solution produces OH^- ions.

Bronsted Lowry Theory

An **acid** is a proton donor

A **base** is a proton acceptor

- A "proton" is an ionized hydrogen atom (H^+)
- This theory is most often used for aqueous solutions of acids and bases but is not limited to them.
- Example: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Lewis Theory

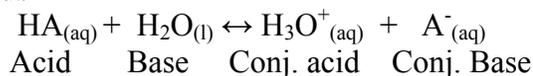
An **acid** is an electron pair acceptor

A **base** is an electron pair donor

Note: For most of the acid-base reactions, we will be using the Bronsted-Lowry definitions.

General Format:

Acids



Conjugate acid is the base plus an attached proton.

Conjugate base is the acid minus a proton.

IE: the acid forms a conjugate base, the base forms a conjugate acid.

This format is usually shortened to $HA_{(aq)} \leftrightarrow H^+_{(aq)} + A^-_{(aq)}$

Acid Dissociation Constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

Bases



Base Dissociation Constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Amphoteric (amphiprotic) substances can act as an acid or base, such as water in the above formats.

STRENGTHS OF ACIDS AND BASES:

Review the list of strong acids and bases.

For strong acids:

- K_a is very large
- The acid almost completely dissociates $[H^+] = [HA]_0$
- A^- is a weak base relative to H_2O

For weak acids:

- K_a is very small
- The acid only partly dissociates $[H^+] \ll [HA]_0$
- A^- is a stronger base than H_2O and mostly remains bound to the proton.
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Summary

- The stronger an acid, the weaker its conjugate base.
- The stronger a base, the weaker its conjugate acid.
- An acid-base reaction is favored in the direction from stronger to weaker.

Binary Acids (HX):

- The relative strength of the acids increase from top to bottom in a periodic group.
- This is due to bond energy and anion size.
- The relative strengths of binary acids increase from left to right across a period.
- This is due to the increase in electronegativity difference between the element and hydrogen.

Oxoacids(HO-E-):

- The strength of the acid depends on the electronegativity of element E and what else is attached to E.
- As the electronegativity increases, the electrons are drawn away from the OH bond, weakening it and allowing it to dissociate more freely, giving a stronger acid.
- If additional oxygen atoms are attached to the element E, they add to its effect, pulling electrons from the OH bond, and further increasing the strength of the acid.

Carboxylic Acids (R-COOH):

- If the R group is a hydrocarbon chain it has little effect on acid strength.
- If the R-group contains atoms with high electronegativity, they can withdraw electrons from the O-H bond, increasing acid strength.
- The strength of the acid will depend on how many high-electronegativity atoms are in the R-group and how close they are to the OH group.

Amines (R-NH₂):

- An R-group which draws electrons from the atom to which the H⁺ bonds will make the base weaker.
- Aromatic amines are weaker than non-aromatic (aliphatic) amines.

THE pH SCALE:

The Self-ionization of Water:



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

K_w is the ion-product constant for water.

At 25 °C, the equilibrium concentrations in pure water are

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}\text{M}$$

Therefore $K_w = 1.0 \times 10^{-14}$ at 25 °C

pH and pOH:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pK} = -\log K$$

Note:

- when you calculate using a log, only the digits after the decimal point are significant.

BUFFERS

Buffer Solution

- Changes pH only slightly when small amounts of a strong acid or strong base are added.
- Contains a weak acid and its salt (conjugate base) or a weak base and its salt (conjugate acid).
- The acid component of the buffer can neutralize small added amounts of OH⁻ and the basic component can neutralize small added amounts of H₃O⁺.

Buffer Capacity

- The ability of a buffer to absorb H⁺ or OH⁻ without significantly changing pH.
- The more buffering material present in the solution, the greater the buffering capacity.
- Buffers are most effective if the concentrations of the acid and its conjugate base are equal.
- Generally, buffers are effective over a pH range one unit on either side of pH=pKa.

Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pK}_a = -\log K_a$$

A^- = conjugate base

HA = weak acid

Henderson-Hasselbalch can be used for buffer solutions where:

- The ratio of $[\text{A}^-]$ to $[\text{HA}]$ has a value between 0.10 and 10.
- Both $[\text{A}^-]$ and $[\text{HA}]$ must exceed K_a by a factor of 100 or more.

$$\text{pK}_a + \text{pK}_b = 14$$

ie: the equation may also be used for basic buffers by converting K_b to pK_a .

ACID-BASE REACTIONS WHEN SALTS DISSOLVE.

Salt = ionic compound

Hydrolysis - the acid-base reaction of ions with water.

1. Salts of strong acids and strong bases form neutral solutions. (Remember, the strong bases are the group 1 and 2 metal hydroxides).
2. Salts of weak acids and strong bases form basic solutions.
3. Salts of strong acids and weak bases form acidic solutions.
4. Salts of weak acids and weak bases may form solutions that are acidic, basic, or neutral.

In summary - Only ions that are the conjugates of weak acids or weak bases hydrolyze appreciably.

TITRATIONS.

Titration - Two reactants are made to react in stoichiometric proportions.

1. A known quantity of one reactant is placed in a beaker with a few drops of indicator.
2. A buret is filled with the other reactant (the titrant).
3. The titrant is slowly added to the beaker until a color change is observed.
4. The volume of the titrant used is recorded.
5. Calculations can now be made to ascertain the concentration etc. of the reactants.

Titration is commonly carried out for neutralization reactions.

Equivalence point - the critical point in the titration where neither the acid nor the base is in excess.

End point - The point in the titration where the indicator changes color.

Acid-Base Indicators.

- Mostly organic molecules that are weak acids.

- Exhibit one color when the proton is attached and another when it is absent (the conjugate base).



Titration Calculations and Titration Curves

Read through all examples and work sample problems from your text. Additional problems will be given in class.

POLYPROTIC ACIDS.

- Acids with more than one hydrogen
- The ionization of each hydrogen occurs separately
- The first dissociation occurs to the greatest extent; subsequent dissociations have much smaller equilibrium constants,
- For most polyprotic acids, the first step is the one to be considered when calculating pH. Subsequent dissociations make little contribution of H^+ ions.