Acids + Bases

Acid Base definitions: The definition of acids and bases has evolved over time.

The word "acid" means sour, referring to the sour taste of weak acids such as citric acid. In the 1880's, chemists Ostwald & Arrhenius proposed the first chemical definition, known as the "Arrhenius definition":

**ACID** - produces protons (H⁺) e.g. HCl → H⁺ + Cl⁻

**BASE** - produces hydroxide ions (OH⁻) e.g. NaOH → Na⁺ + OH⁻

This definition is limiting because it requires an aqueous solution (i.e., the solvent must be water) and requires either an ionizable proton or a source of hydroxide ions. When an Arrhenius acid is combined with an Arrhenius base, neutralization occurs.

neutralization: acid + base → salt + H₂O

example: HCl(aq) + NaOH(aq) → NaCl(aq) + H₂O(l)

* Arrhenius was awarded the Nobel prize for work related to his definition of acids & bases.

Brønsted and Lowry proposed their definitions in 1923 based on the idea that a proton is transferred during an acid-base reaction.

**Brønsted-Lowry**

**ACID** - proton donor (H⁺) e.g. HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)

**BASE** - proton acceptor e.g. NH₃(aq) + H₂O(l) → NH₄⁺(aq) + OH⁻(aq)

An important benefit of this definition is that the proton is transferred from an acid to a base, so both must be present. This definition is more general because it does not require an aqueous solution. It does, however, require an ionizable proton. The products in this case are not salt and water.
but rather a conjugate acid and conjugate base. For example,

\[ \text{CH}_3\text{COOH} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{CH}_3\text{COO}^- \]

\( \text{CH}_3\text{COOH} \) and \( \text{NH}_3 \) are the conjugate acid-base pairs.

Notice that I used a double arrow. This is because weak acids and bases do not completely dissociate, and an equilibrium is established between reactants (acid, base) and products (conjugate acids, bases). This definition is the one you will work with the most in this course.

An even more general definition is the "Lewis definition," also proposed in 1923.

\[ \boxed{\text{ACID}} - \text{electron acceptor} \quad \text{e.g.} \quad \text{H}^+ + 2\text{NH}_3 \rightarrow \text{NH}_4^+ \quad \text{adduct} \]

\[ \boxed{\text{BASE}} - \text{electron donor} \quad \text{Ag}^+ + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ \quad \text{adduct} \]

In this definition, electrons are transferred, typically to form a bond. The resulting complex is known as an adduct.

**Acid/Base Strength**

The strength of an acid is determined by the concentration of [H\(^+\)] in solution because it is indicative of the % dissociation of the acid.

\[ \text{HA(aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq) \]

\( K_a = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]} \)

The greater the concentration of [H\(^+\)], the farther to the right lies the equilibrium, i.e., the stronger the acid.

Strong acids have large \( K_a \)
Strong Acids

There are seven strong acids that you need to know:

- $\text{H}_2\text{SO}_4(\text{aq})$ - sulfuric acid
- $\text{HCl}(\text{aq})$ - hydrochloric acid
- $\text{HNO}_3(\text{aq})$ - nitric acid
- $\text{HClO}_4(\text{aq})$ - perchloric acid
- $\text{HI}(\text{aq})$ - hydroiodic acid
- $\text{HBr}(\text{aq})$ - hydrobromic acid
- $\text{HOClO}_3(\text{aq})$ - chloric acid

*Note: not universally accepted as a strong acid.*

These acids are strong because $K_a \gg 1$

$$\text{HA}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq}) \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

At equilibrium $[\text{HA}]$ is very small, and $[\text{H}^+]$ and $[\text{A}^-]$ are very large. For the seven strong acids we can assume 100% dissociation.

$[\text{HA}]_{\text{init}} \approx [\text{H}^+]_{\text{eq}}$

14:31

The pH Scale

Because $[\text{H}^+]$ concentrations are very low ($10^{-4}$ to $10^{-1}$) and range over many factors of 10, it is convenient to talk about $[\text{H}^+]$ in terms of the exponent, or pH.

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

It follows that pH of a solution of strong acid can be determined from the initial concentration of the acid.

*Learn how to deal with significant figures in log functions!*

14-17, 14-47, 14-50,

Note: as acid strength increases, pH decreases!
Before we can consider weak acids, we must first look at the autoionization of water. At 298K, a small % of water molecules will dissociate to produce protons and hydroxide ions:

\[ H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \text{Kw} = [OH^-][H^+] \]

\[ \text{dissociation constant in water} \]

I should note that H⁺ is a theoretical construct. In reality, H⁺ is much too reactive to be floating around in solution on its own. The positive charge is much more likely to be associated with a water molecule. In fact, we know that H⁺ ions are found in solution as a part of a water cluster. e.g. \( H_3O^+ \) or \( H_5O_2^+ \), we use \( H_3O^+ \) and H⁺ concentrations interchangeably because they are the same.

\[ H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad \text{Kw} = [OH^-][H_3O^+] \]

\[ H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \text{Kw} = [OH^-][H^+] \]

@ 298K, Kw = 10⁻¹⁴, since \( H_3O^+ \) and OH⁻ have a one-to-one stoichiometric ratio, we can calculate the concentrations of each by:

\[ 10^{-14} = [OH^-][H_3O^+] = (10^{-7})M(10^{-7})M \]

and from our expression for pH:

\[ \text{pH} = -\log (10^{-7}) = 7 \]

-I am sure you all know that pH of a neutral solution at 298K is 7.

* The auto dissociation equilibrium must be considered w/ weak acids because of its contribution to pH.
For acidic solutions $[H^+] > 10^{-7}$ so $pH < 7$ and for basic solutions $[OH^-] < 10^{-7}$ and $pH > 7$.

A useful relationship:

$$K_w = [H^+] [OH^-]$$

$$-\log K_w = -\log [H^+] + (-\log [OH^-]) \quad pK_w = pH + pOH$$

Bases: when a base interacts with water, the following equilibrium is established.

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \quad K_B = \frac{[OH^-][HB^+]}{[B]}$$

If the base is very strong, the equilibrium lies far to the right.

$$B(aq) + H_2O(l) \rightarrow HB^+(aq) + OH^-(aq) \quad K_B \gg \gg 1$$

And we can assume that $[B]_{init} = [HB^+]_{eq} = [OH^-]_{eq}$

Typical strong bases are ionic salts of hydroxide.

*E.g.* NaOH, Ca(OH)$_2$, KOH
The relationship between $K_a$ and $K_b$

\[
K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad \text{and} \quad K_b = \frac{[HA][OH^-]}{[A^-]}
\]

\[
2H_2O(l) \rightleftharpoons H_3O^+ + OH^- \quad K_w = K_a \cdot K_b
\]

proof

\[
\left(\frac{[A^-][H_3O^+]}{[HA]}\right)\left(\frac{[HA][OH^-]}{[A^-]}\right) = \frac{[H_3O^+][OH^-]}{K_w}
\]

The autoionization equilibrium can be discounted for strong acids in aqueous solution because the contribution to $[H^+]$ from the acid is much greater than the contribution from the acid. Weak acids, on the other hand, might need to consider $K_w$.}

\[\text{© 14:20, 14:74}\]