

Classification of Reagents in Chemistry I:

Acids and Bases

- There are 3 definitions of acids and bases. All three are used in both general and organic chemistry depending on the context.
- Acids and bases will undergo neutralization type reactions when mixed. The exact process of the neutralization depends on the type of acids/bases used.

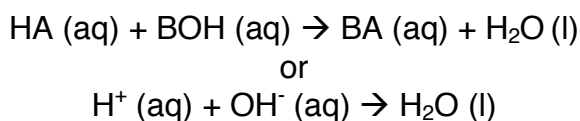
Arrhenius Acids and Bases:

- Arrhenius' definition of acids and bases is the most restrictive definition. But it does include all of the classic strong acids/strong bases we see in general chemistry, and most of the common acids and bases that function in water.

Arrhenius Acids – donate H^+ (hydrogen ion) in water and have H in their formula.

Arrhenius Bases – donate OH^- (hydroxide ion) in water and have OH in their formula

Neutralization – mixing an acid and a base produces a salt and water. The net ionic equation for all Arrhenius neutralizations is formation of H_2O .



Strong vs. Weak – Arrhenius acids and bases are often referred to as 'strong' or 'weak'. This refers to the amount of separation into ions in the aqueous solution. A 'strong' acid or base is a strong electrolyte and fully dissociates into ions in aqueous solution. A 'weak' acid or base is a weak electrolyte and only partially dissociates into ions in aqueous solution.

Common Strong Acids:

HCl (aq) , HBr (aq) , HI (aq) , $\text{HNO}_3 \text{ (aq)}$, $\text{HClO}_4 \text{ (aq)}$, $\text{H}_2\text{SO}_4 \text{ (aq)}^*$

Common Weak Acids:

$\text{CH}_3\text{COOH (aq)}$, RCOOH (aq) , HF (aq) , $\text{HNO}_2 \text{ (aq)}$, $\text{H}_3\text{PO}_4 \text{ (aq)}$, $\text{H}_2\text{S (aq)}$, HCN (aq)

Common Strong Bases:

NaOH (aq), KOH (aq), LiOH (aq), RbOH (aq), CsOH (aq), Na₂O (aq), K₂O (aq)

Common Weak Bases:

Ba(OH)₂ (aq), Ca(OH)₂ (aq), Sr(OH)₂ (aq), NH₄OH (aq)**

* H₂SO₄ is a polyprotic acid, the first loss of H⁺ is a strong acid (full dissociation in water), the second is a weak acid (only partial dissociation in water).

** NH₄OH (aq) as such does not truly exist. The convention for writing NH₄OH is a holdover from the original Arrhenius definition that requires the OH⁻ in the formula. In aqueous solution the weak base NH₃ (aq) is in equilibrium with NH₄⁺(aq) and OH⁻(aq), and NH₄OH (aq) as a species does not exist. Modern texts often simply write NH₃ (aq), but it is still traditionally considered as an Arrhenius base.

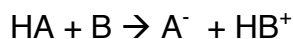
Bronsted-Lowry Acids and Bases:

- Bronsted and Lowry's definition of acids and bases becomes more permissive by removing water as the solvent somewhat increasing what can be considered an acid and by greatly expanding what can be considered a base. This is the most commonly used definition of acids and bases in typical general and organic chemistry classes.

Bronsted-Lowry Acids – donate H⁺ (hydrogen ion)

Bronsted-Lowry Bases – accept H⁺ (hydrogen ion) (Bases have some sort of lone pair and can be neutral or anions.)

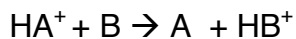
Neutralization – Mixing an acid and a base produces a conjugate acid and a conjugate base. A conjugate pair differs by H⁺ the conjugate acid has an extra H⁺ that the conjugate base lacks. Water is still often used as a solvent, but it's no longer the only possible solvent for an acid base reaction, and neutralization reactions can take place in any solvent or even in gas phase.



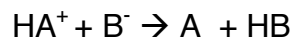
or



or



or



Strong vs. Weak – Bronsted-Lowry acids and bases are referred to as 'stronger' or 'weaker' rather than the absolutes of 'strong' and 'weak'. We now have a continuous scale of strengths (pK_a 's) rather than a single differentiation point.

Common Acids: HCl , H_2SO_4 , H_3PO_4 , HF , H_2CrO_4 , RCOOH , H_2S , RNH_3^+ , HCN , H_2O , ROH , NH_3 , R-NH_2

Common Bases: R-Li , NaNH_2 , KH , RONa , NaOH , KCN , NaHCO_3 , RCOONa , KHSO_4 , NaCl

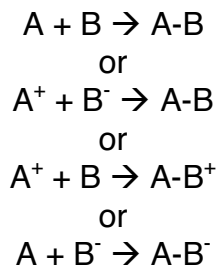
Lewis Acids and Bases:

- Lewis Acids and bases become more permissive by no longer requiring there to be a hydrogen ion (H^+) transferred. Anything similar to H^+ is permitted to act as an acid, thus greatly expanding the definition of an acid. Anything that was a Bronsted-Lowry base is now still a Lewis base simply no longer required to accept only H^+ .

Lewis Acids – Accept a lone pair of electrons into an empty orbital. (Acids are generally cations or trigonal planar $6e^-$ species).

Lewis Bases – Donate a lone pair of electrons into an empty orbital. (Bases have some sort of lone pair and can be neutral or anions.)

Neutralization – Mixing an acid and a base produces a new covalent bond between the acid and the base. We form an adduct. Neutralization reactions can take place in solution or in gas phase and the solvent may or may not be water.



Strong vs. Weak – The strength of Lewis acids and bases does not generally come up often in basic general or organic chemistry. Comparisons can be done by looking at the enthalpy of formation of the adduct. A more exothermic reaction implies stronger acids/bases.

Common Acids: $\underline{\text{H}}^+$, $\underline{\text{Zn}}^{2+}$, $\underline{\text{Fe}}^{3+}$, $\underline{\text{CH}}_3^+$, $\underline{\text{B}}\text{H}_3$, $\underline{\text{B}}\text{F}_3$, $\underline{\text{Al}}\text{Cl}_3$, $\underline{\text{Fe}}\text{Br}_3$.

Common Bases: $\underline{\text{R}}\text{-Li}$, $\text{Na}\underline{\text{N}}\text{H}_2$, $\text{K}\underline{\text{H}}$, $\text{R}\underline{\text{O}}\text{Na}$, $\text{Na}\underline{\text{O}}\text{H}$, $\text{K}\underline{\text{C}}\text{N}$, $\text{NaH}\underline{\text{C}}\underline{\text{O}}_3$, $\text{RCO}\underline{\text{O}}\text{Na}$, $\text{K}\underline{\text{H}}\underline{\text{S}}\underline{\text{O}}_4$ $\text{Na}\underline{\text{C}}\underline{\text{l}}$

- *Note:* H^+ is considered a Lewis acid, but by strict definition HCl would not be! HCl simply produces the active H^+ .
- *Note:* The definition of what can be classified as a Lewis acid can be quite complicated as few Lewis acids exist in pure form outside of a gas phase. Modern understanding of Lewis acids and bases requires a discussion in molecular orbital theory that is beyond the scope of this course. E.g. BH_3 really exists as B_2H_6 with bridging H between the two B atoms!

Classification of Reagents in Chemistry II: Dealing with pK_a

pK_a and K_a – Generally acid strengths for Bronsted-Lowry (and Arrhenius) acids are written as K_a (acid dissociation constant) or pK_a values and base strengths for Bronsted-Lowry (and Arrhenius) bases are written as K_b (base dissociation constant) or pK_b values. Stronger acids have large K_a and small pK_a and stronger bases have large K_b and small pK_b . Most K_a and K_b are measured as the amount of dissociation in aqueous solution (it's still convenient) and the K_a and K_b of very strong or very weak acids or bases are extrapolated from dissociation measured in different solvents. Because there are many orders of magnitude to K_a and K_b generally the log (pK_a/pK_b) scale is used.

Dissociation Eq'n	Aqueous Dissociation Eq'n	Log Eq'n
$K_a = [H^+][A^-] / [HA]$	$(K_a = [H_3O^+][A^-] / [HA][H_2O])$	$pK_a = -\log(K_a)$
$K_b = [HB^+] / [H^+][B]$	$(K_b = [OH^-][HB^+] / [B][H_2O])$	$pK_b = -\log(K_b)$

K_a vs. K_b – There is a relationship between K_a and K_b in a conjugate pair, the stronger the acid the weaker the conjugate base and vice versa. A stronger acid wants to lose an H^+ so its conjugate base is weaker, the conjugate base is not eager to get the H^+ back (it just worked hard to lose it!). A weaker acid wasn't willing to lose H^+ in the first place so its conjugate base will be willing to regain H^+ and its conjugate base will be stronger. The relationship between K_a and K_b can be seen by looking at K_w (auto-ionization of water).

$$K_a \times K_b = ([H_3O^+][A^-] / [HA][H_2O]) \times ([OH^-][HB^+] / [B][H_2O])$$

If $HA = HB^+$ and $A^- = B$ as in a conjugate pair this equation can be simplified

$$K_a \times K_b = ([H_3O^+]/[H_2O]) \times ([OH^-]/[H_2O]) = [H_3O^+][OH^-]/[H_2O]^2 = K_w$$

($K_w = 1.0 \times 10^{-14}$ at 298 K)

So regardless of which conjugate pair we're looking at:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

And thus as K_a increases (stronger acid) K_b decreases (weaker base).

- Most of the time in general and organic chemistry we work with the pK_a value and extrapolate the pK_b value only if necessary.

Strong vs. Weak. – The terms **strong** and **weak** acids or bases are often used with Arrhenius acids and bases. Where a strong acid or base has nearly 100% dissociation into free ions in water and a weak acid or base has only partial dissociation into free ions and the major portion of the acid or base stays molecular or in solid form if ionic. Strong acids will have a $pK_a < 0$ and a $K_a > 1$, while strong bases will have a $pK_b < 0$ ($pK_a > 14$) and a $K_b > 1$.

This is not to be confused with the similar terms **stronger** and **weaker** acids and bases that are used to compare the relative pK_a or pK_b of Bronsted-Lowry acids and bases. An acid (or base) may be 'stronger' than another while both are still weak acids (or bases). E.g. HF ($pK_a = 3.2$) is a stronger acid than HCN ($pK_a = 9.3$), but both are weak acids with $pK_a > 0$. One common source of confusion for organic chemistry students is the new prevalence of strong bases. Bronsted-Lowry allows many more options for bases, quite a few of which are strong bases, but all strong bases do not have the same strength so sometimes a strong base is still not strong enough. E.g. Hydroxide ion (OH^- , pK_a of $H_2O = 15.7$) is a strong base as is amide ion (NH_2^- , pK_a of $NH_3 = 36$), however hydroxide ion is not a strong enough base to deprotonate ammonia to form amide ion.