

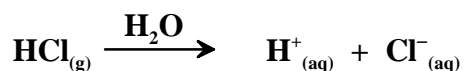
Acid Base Concepts

The Swedish chemist, Svante Arrhenius, framed the first successful concept of acids and bases. He defined acids and bases in terms of their effect on water. According to Arrhenius, acids are substances that increase the concentration of H^+ ions in aqueous solution, and bases increase the concentration of OH^- ions in aqueous solution.

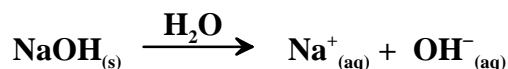
But many reactions that have characteristics of acid-base reactions in aqueous solution occur in other solvents or no solvent at all. The Bronsted-Lowry and Lewis concepts of acids and bases apply to nonaqueous as well as aqueous solutions and also enlarge on the Arrhenius concept.

Arrhenius concept

acids: Hydrogen ion (H^+) donors

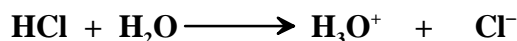


Bases: Hydroxide ion (OH^-) donors.



Hydronium Ion

In reality, H^+ ions do not float around in aqueous solution. Instead, they always attach themselves to a water molecule forming the *hydronium ion*, H_3O^+ . So a more accurate representation of the dissociation of HCl above would be:

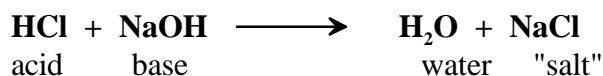


For simplicity's sake, many texts will leave the water out of these dissociation equations assuming that the student knows that $\text{H}^+_{(aq)}$ really means $\text{H}_3\text{O}^+_{(aq)}$.

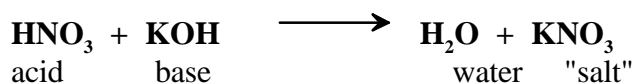


In the Arrhenius concept, when an acid and a base are mixed, the result is water (formed from the H^+ and the OH^-) and a "salt" (composed of the leftover cation of the base and the leftover anion of the acid).

For example



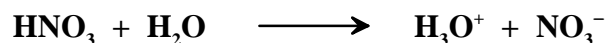
This type of neutralization reaction occurs with any Arrhenius acid and base.



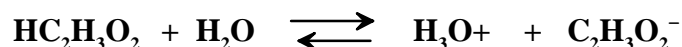
Strong vs. Weak Acids

When acids readily give up their H^+ ions to solution they are considered to be "strong acids". There are only six acids that ionize so near to completely as to be considered strong acids. These include: **HCl, HBr, HI, HNO₃, H₂SO₄, and HClO₄.**

These acids dissociate 100% in aqueous solution, consequently a 'single' arrow is used when illustrating their behavior in water. For example



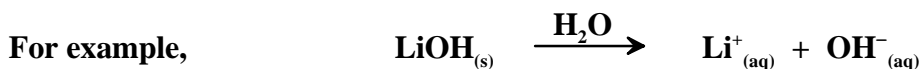
All other acids do not ionize sufficiently to be called strong. These acids establish an equilibrium with water and consequently are represented with a 'double' arrow. For example;



The equilibrium would suggest incomplete dissociation, characteristic of weak acids.

Strong vs. Weak Bases

Just as with the acids, only six hydroxide bases ionize completely enough in water as to be considered strong. These include **LiOH, NaOH, KOH, RbOH, CsOH, and Ba(OH)₂.** These six bases ionize 100% in aqueous solution. Again, like the strong acids, this is conveyed by using a 'single' arrow in their equations.



However some hydroxide bases do not ionize completely in aqueous solution and are considered weak bases. This incomplete ionization is again conveyed by representing the ionization as an equilibrium.



The Bronsted Lowry Concept.

In the Bronsted-Lowry concept of acids and bases, the definitions are slightly different. Here, we view a "base" as any compound or ion *that will accept an H^+* , that is, remove an H^+ from solution (in essence, neutralizing it)

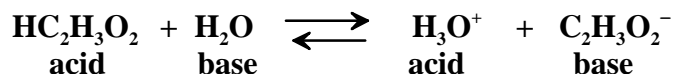
acid: hydrogen ion donor

base: a hydrogen ion acceptor.

This concept introduces the idea of "conjugate acid-base pairs". That is, if an acid loses its H^+ , the resulting anion is now in a position to re-accept a proton making it a Bronsted-Lowry Base. The acid and its corresponding anion are considered a *conjugate acid-base pair*.

Logically, if an acid is considered strong, its conjugate base (that is, its anion) would be weak, since it is unlikely to accept a hydrogen ion.

For example;



In this case, on the left of the arrow, the $\text{HC}_2\text{H}_3\text{O}_2$ is a potential proton donor (acid) and the water is the potential proton acceptor (base). On the right side of the arrow however, the H_3O^+ is now a potential proton donor (acid) and the acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, is now a potential proton acceptor (base). So, in essence, *the $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$ are a conjugate acid-base pair* where $\text{HC}_2\text{H}_3\text{O}_2$ is the acid (with the H^+ to give) and the $\text{C}_2\text{H}_3\text{O}_2^-$ is the base (with the potential to take back the H^+).

Likewise, the H_2O and the H_3O^+ are a conjugate pair with H_3O^+ representing the potential H^+ donor (the acid) and H_2O acting as the potential recipient of the H^+ (the conjugate base). So in this equilibrium, we have two opposing Bronsted-Lowry acid base reactions.

In this particular example, H_3O^+ is the stronger of the two acids, consequently, the equilibrium is skewed to the left favoring the formation of reactants ($\text{HC}_2\text{H}_3\text{O}_2$ and H_2O). The following table outlines the relative strength of some common acids and their conjugate bases.

This concept of conjugate acid-base pairs is fundamental to understanding why certain salts can act as acids or bases in solution.

	Acid	Base	
Strongest acids	HClO_4	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
↓	HI	I^-	↑
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_3	H_2PO_4^-	
	HNO_2	NO_2^-	
	HF	F^-	
	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	
	$\text{Al}(\text{H}_2\text{O})_6^{+3}$	$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HClO	ClO^-	
	HBrO	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
HS^-	S^{2-}		
Weakest acids	H_2O	OH^-	Strongest bases

Lewis Concept of acids and bases

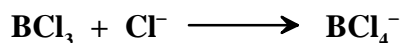
In the Lewis concept, an acid is not a proton donor, but instead is an electron acceptor. The bases in this concept are electron donors.

acid: electron acceptor

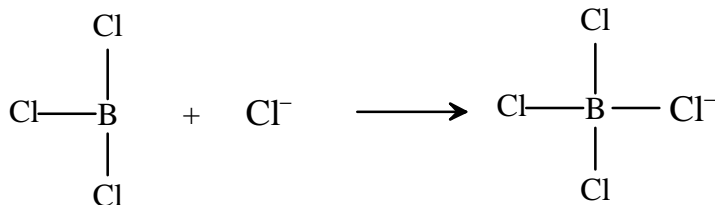
base: electron donor.

This concept seems to cover those reactions that behave as if they are an acid base neutralization reaction but don't seem to involve H^+ ions.

For example, the reaction of BCl_3 with Cl^- reacts as follows.



If we represented this as Lewis structures,

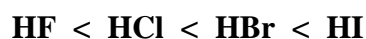


we see that the Cl^- ion is donating the electrons to form the bond with BCl_3 which is accepting those electrons. So in the Lewis sense, the Cl^- is the Lewis base while the BCl_3 (the electron acceptor) is acting as the Lewis acid.

Molecular Structure and Acid Strength

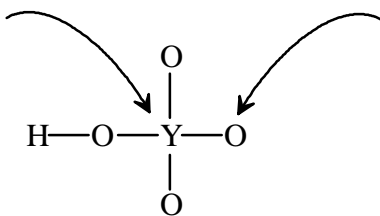
If we look at a "generic" acid....let's call it H-X, it is logical to assume, that the weaker or more polar the bond is between the H and the X, the more H^+ will be released and the acid will be stronger in solution.

For example, in the series of acids, HF, HCl, HBr, and HI, the bond strength decreases as we go from HF to HI, making HI the strongest acid in the series and HF the weakest acid. That is,



If we look at the oxoacids, those acids whose anions contain oxygen (such as HNO_3 or H_2SO_4) we see that the *electronegativity of the central atom* is most critical in determining how easily the H^+ can dissociate. If the electronegativity of the central atom is great, this weakens the bond between the oxygen and the Hydrogen atom, allowing the Hydrogen to easily break free as H^+ .

The more electronegative "Y" becomes, the more electrons are drawn away from the O-H bond allowing the H^+ to break away easier.



Likewise, the more electron withdrawing oxygen atoms that are attached to "Y" weaken the O-H bond allowing the H^+ to break away easier

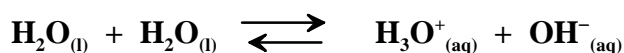
For example:



This can explain why H_2SO_4 is a stronger acid than H_2SO_3 (due to the presence of more oxygens in H_2SO_4) or that $HClO_4$ is a stronger acid than HIO_4 (since chlorine is more electronegative than iodine).

Self Ionization of Water

Pure water, although considered a nonelectrolyte, does contain a small number of ions. This results from the *self-ionization of water, a reaction in which two like molecules react to give ions*. The self-ionization of water involves the transfer of a proton (H^+) from one water molecule to another.



The equilibrium expression for this equation would be

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

Because the concentration of ions is very small, the concentration of water remains virtually constant at 55.56 M. If we rearrange the equation above to put $[\text{H}_2\text{O}]^2$ with K_c , we get:

$$[\text{H}_2\text{O}]^2 K_c = [\text{H}_3\text{O}^+][\text{OH}^-]$$

(constant)

We call the equilibrium value of the ion product $[\text{H}_3\text{O}^+][\text{OH}^-]$ the ion-product constant for water, which is written K_w . At 25°C, the value of K_w is 1.0×10^{-14} . Note: like any equilibrium constant, K_w changes with temperature. At body temperature, 37°C, K_w equals 2.5×10^{-14} .

Since $[\text{H}^+]$ is usually substituted for $[\text{H}_3\text{O}^+]$, the ion-product expression for water can be written:

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

If we consider pure water, it's a simple step to see that $[\text{H}^+]$ must equal $[\text{OH}^-]$, therefore these concentrations are *both* 1.0×10^{-7} .

If you add an acid or a base to water, the concentrations of H^+ and OH^- *will no longer be equal*. The equilibrium constant equation will still hold, however, such that *as one concentration increases, the other decreases*.

Solutions of a Strong Acid or Base

Consider a 0.10 M HCl solution. Since HCl is a strong acid and *dissociates completely*, the reaction below will produce a solution **containing 0.10 M H^+** . Now consider the concentration of H^+ produced by the self-ionization of water. In pure water the H^+ concentration is 1.0×10^{-7} ; in an acid solution, it is even smaller. You can see this by applying Le Chatelier's Principle to the self-ionization of water.



Consequently, the concentration of H^+ produced by the self-ionization ($< 1.0 \times 10^{-7}$ M) is negligible in comparison to that produced by the HCl (0.10 M). *So, 0.10 M HCl has a concentration of H^+ ion equal to 0.10 M.*

In a solution of strong acid, you can *usually ignore the H^+ provided by the self-ionization of water*. However, in very dilute solutions of acid, for example 1.0×10^{-7} M HCl, the self-ionization of water provides approximately the same amount of H^+ to the solution and *cannot be ignored*.

Note that although the solution above is very acidic, the self-ionization equilibrium expression still holds. This accounts for the small concentration of OH^- ions still found even in acidic solutions.

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

$$1.0 \times 10^{-14} = 0.10 \times [\text{OH}^-]$$

Solving for $[\text{OH}^-]$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}$$

The OH^- concentration is 1.0×10^{-13} M

Now consider a solution of strong base, such as 0.10 M NaOH. Because NaOH is a strong base, it completely ionizes in aqueous solution to provide 0.10 M OH^- ions. The concentration of OH^- produced by the self-ionization of water ($<1.0 \times 10^{-7}$ M) is negligible and can be ignored.

In a solution of strong base, you can *usually ignore the OH provided by the self-ionization of water*. However, in very dilute solutions of base, for example 1.0×10^{-7} M NaOH, the self-ionization of water provides approximately the same amount of OH^- to the solution and *cannot be ignored*.

Note that although the solution above is very basic, the self-ionization equilibrium expression still holds. This accounts for the small concentration of H^+ ions still found even in acidic solutions.

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

$$1.0 \times 10^{-14} = [\text{H}^+] \times 0.10$$

Solving for $[\text{H}^+]$

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}$$

The H^+ concentration is 1.0×10^{-13} M

pH, POH

Although you can quantitatively describe the acidity of a solution by giving the hydrogen-ion concentration, it is often more convenient to give the acidity in terms of **pH**, which is defined as *the negative of the logarithm of the molar hydrogen-ion concentration*.

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

For example, a solution whose hydrogen ion concentration is 1.0×10^{-4} has a pH of:

$$\mathbf{pH = -\log (1.0 \times 10^{-4}) = 4.0}$$

A neutral solution whose hydrogen ion concentration is 1.0×10^{-7} at 25°C , has a pH of 7.00. *For an acidic solution, the hydrogen ion concentration is greater than 1.0×10^{-7} , so the pH is less than 7.00.*

Similarly, *a basic solution has a pH greater than 7.00.*

A measurement of hydroxide ion concentration, similar to pH, is the **pOH**. This is defined as *the negative of the logarithm of the hydroxide ion concentration*.

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

Then, because $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25°C , you can show that

$$\mathbf{pH + pOH = 14.00}$$

CHEM 2**Chapter 15 Assignments**

The following problems will be collected at the first exam.

Review Questions: 1,4,7,11,12,13,19

Problems: 23,27,29,37,41,45,49,53,57,61,65,69,79,81,85,89

Exam Review Topics**terms**

Acid (Bronsted-Lowry)
Base (Bronsted-Lowry)
Conjugate acid-base pair
Amphiprotic
Lewis Acid
Lewis Base
Self-ionization
Ion-product constant for water
pH, pOH

skills/operations

Identifying acids and bases
Identifying Lewis acids and bases
Determining relative strengths of acids and bases
Calculating $[H^+]$ and $[OH^-]$
Calculating pH and pOH