

Acids and Bases:

What is an "Acid"? - We are very aware of things being called acids. Lemon juice's sour taste is attributed to an acid (citric acid). In fact, the word acid comes from the Greek or Latin for sour. Acids have been known for a very long time, but it wasn't till about 100 years ago that the nature of common acids was discovered. Swante Arrhenius (the activation energy guy from Chapter 7) did experiments and postulated that the acids all have one thing in common. His definition is:

Any substance that produces H^+ when placed in water is an acid.

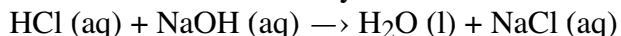
It took a few years before people accepted this definition, but, eventually, they did. As we will see, once chemical bonding and molecular structures were understood, the rather narrow definition given above falls short of the mark.

What is a "Base"? - Bases, also known as alkalis (because of the predominance of bases that contain alkali (group IA) metal ions), have also been known. While acids invoke images of burning, bases don't seem to have the same mystique. In fact, bases, when touched, feel slippery. Also, if we were to taste a base (and I DO NOT recommend this) it would be bitter rather than sour. Arrhenius noticed that when acids and bases mixed, they produced a salt and water. The formula for water, H_2O , was known at the time, so Arrhenius surmised the following definition:

Any substance that produces OH^- when placed in water is a base.

In other words, in order to produce water from H^+ , one must combine it with OH^- . A very common base is lye. It has been used for many years to make soap, unclog drains, and cause violent deaths when fed to unsuspecting enemies. The chemical name for it is sodium hydroxide, i.e. NaOH. As we can see, this is an alkali metal ion (Na^+) and the hydroxide ion (OH^-).

Acid-Base Neutralization: The definitions above, taken together, are called the Arrhenius Acid-Base Theory. They were the first attempt at understanding the nature of acids and bases. Built into the definitions is the experimental fact that when an acid and a base react they produce water and a salt. This reaction is called **acid-base neutralization**. The salt, therefore, is the product of combining the negative ion from the acid with the positive ion from the base. A very common acid-base neutralization is:



Here, the chloride ion from hydrochloric acid and the sodium ion from sodium hydroxide combine to form sodium chloride, common table salt.

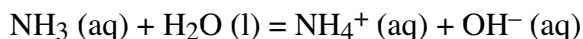
Modification of the Definitions: Brønsted-Lowry - The Arrhenius definitions, once accepted, were considered to be the greatest achievement in chemistry. However, there were certain experimental results that caused some people concern. Namely, it was known that ammonia, $NH_3(g)$, when dissolved in water, acts like a base. Clearly, there are no OH^- s in ammonia! Supporters of Arrhenius' theory decided that when ammonia mixed with water, a new compound was formed called ammonium hydroxide, NH_4OH , which does, in fact, have the requisite OH^- . However, now that we know all about Lewis

structures and molecular bonding, we realize that there is no way of drawing a Lewis structure for ammonium hydroxide as a molecule.

In the early part of the century, two chemists tried to understand this issue, and came up with a more general definition of an acid and a base. These two guys were named Brønsted and Lowry. Like Arrhenius, they liked the idea of an acid producing an H^+ . However, they realized that the free H^+ in solution is not absolutely necessary for the acid characteristic to be present. Rather, as long as the compound CAN produce an H^+ , it is an acid.

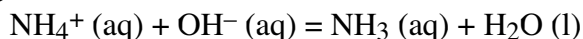
Similarly, the definition of a base had to be modified. Arrhenius' definitions were based on the production of water in a neutralization reaction. Brønsted and Lowry thought that the water, and consequently, the OH^- , was only one possible product. They said that **the purpose of the base is to accept the H^+** from the acid. Since the Arrhenius OH^- can accept an H^+ (to produce H_2O), it is a Brønsted-Lowry (B-L) base as well. And, as in the discussion of redox reactions, where we said that you can't have an oxidation without a reduction occurring simultaneously, in the B-L theory, you can't have an acid forming its conjugate base without a base forming its own conjugate acid!

How does the B-L theory explain ammonia? - The big triumph of the B-L definition is that it explains the ammonia phenomenon very elegantly. According to the new definitions, the reaction between water and ammonia is as follows:



Notice, the H_2O is donating an H^+ to the base NH_3 . Thus, H_2O in this case is an acid!

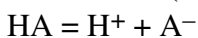
The equilibrium sign implies that the reaction can go in the opposite direction. If we write it that way, we get:



In this case, the NH_4^+ is donating an H^+ to the base OH^- . The relationship between H_2O and OH^- (and between NH_4^+ and NH_3) is called a Brønsted-Lowry **Conjugate Acid/Base Pair**. In B-L terms, neutralization is when an acid and a base form their conjugates.

Relative Strengths - There is an interesting relationship between the conjugate acid and base. The strength of the acid is inversely proportional to the strength of its conjugate base. So, if the acid is strong, the conjugate base is weak, and vice versa. However, we haven't defined what is meant by strong and weak!

The definition of a strong acid is one that donates its H^+ (nearly) completely. In other words, if we abbreviate an acid as HA , where A^- is the conjugate base, and the dissociation (i.e. the donation of the H^+) follows the reaction:

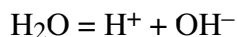


then, if the equilibrium constant for this reaction is extremely large ($K > 1$), the acid is considered strong. On the other hand, if the equilibrium constant is small ($K < 1$), the acid is considered weak. Between two acids, the one with the larger K is the stronger acid.

Similarly, the reverse reaction, i.e. $H^+ + A^- = HA$, will have an equilibrium constant of $1/K_{acid}$. If K_{acid} is small, the $1/K$ will be large, and vice versa.

We have not taken into account the need for (or the presence of) the base that is required to have a B-L neutralization.

Water - From our definition of acids and bases, we see that H_2O fits the bill for the reaction above. In other words,



So, water is the acid, and OH^- is the conjugate base. What accepts the H^+ ? What is the base?

If nothing else is present, another H_2O will accept the H^+ ! The explanation of this requires us to define the B-L base a little more carefully. So far, all we have said is that it "accepts the H^+ ". It was not until Lewis came up with his structures that this was understood. By the way, the explanation we are about to give is also called the "Lewis Base" definition.

When Lewis developed his method for drawing structures, he started analyzing the structures of common acids and bases in search of a pattern. What he found was that the common thread between all the bases was that they had an electronegative center that possessed at least one lone pair of electrons. Lewis assumed that the H^+ was attracted to the negatively charged lone pair. The more attractive the lone pair is, the stronger the base.

This can be used to explain the question above. We will do this symbolically, using Lewis structures:



Thus, water is an acid with OH^- as its conjugate base, BUT it is also a base with H_3O^+ as its conjugate acid!

Recap: Acids and bases are substances that behave certain ways in solution. The Arrhenius definition of an acid is a substance that produces H^+ in solution, and a base is one that produces OH^- . Brønsted and Lowry modified the definition to generalize the definition of a base; they said that a base is any substance that can accept an H^+ in solution.

Auto-ionization of Water: In the Brønsted-Lowry (B-L) definition, an acid must donate its H^+ to a base. In the absence of any other base, the only one there must be the water: $HA + H_2O \rightarrow H_3O^+ + A^-$.

Similarly, a base must accept an H^+ from an acid. In the absence of any other acid, the only acid present is water: $B + H_2O \rightarrow OH^- + HB^+$.

Since water acts as both an acid and a base, two water molecules together can interact with each other in an acid/base reaction: $H_2O + H_2O = OH^- + H_3O^+$. This is called the auto-ionization of water. The equilibrium constant for this reaction is:

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

But, since the concentration of liquid water is constant (since the volume of "solution" is the volume of the solvent - water), we can write:

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$$

This K_w is called the "water constant".

The relative strengths of acids and bases in water are, therefore, based on the water constant. When the equilibrium constant for an acid reaction is larger than K_w , the acid is relatively strong. The larger it is, the stronger the acid. Same with bases. However, by convention, when the acid (or base) constant is less than 1, we refer to the acid as a weak acid (or, for bases, we call them weak bases).

Conjugate Acid/Base Pairs: In the B-L theory, the reaction between an acid and a base produces another acid and base, said to be the **conjugates** of the originals. The relationship between the acid constant of a weak acid and the base constant of its conjugate weak base is:

$$K_w = K_a^{conj} K_b^{conj}$$

This means that if the acid is relatively strong, the conjugate base will be relatively weak.

The pH scale, and pK_a - Since pure water contains no source of H^+ other than water, and no source of OH^- other than water, AND, since the value of K_w is 10^{-14} , the concentrations of H^+ must equal the concentration of OH^- , i.e.

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$$

Thus, in a neutral solution, the concentration of H^+ is 10^{-7} M. For acids stronger than water, the concentration of H^+ is greater than 10^{-7} M.

Since this (10^{-7}) is a difficult number to work with (it is a very small number), it is convenient to take the negative logarithm of it: **$-\log[H_3O^+]$** . When we do this, we get a quantity called the **pH**. The pH scale, therefore, is a way of describing the strength of an acid relative to water. The pH of neutral water is 7. As the concentration of H^+ gets larger, the pH gets smaller. So, **$pH < 7$ means the solution is acidic**.

Similarly, since the $[OH^-] = K_w/[H_3O^+]$, the lower the concentration of H^+ , the higher the concentration of OH^- , i.e. the more basic the solution. This corresponds to a **$pH > 7$ being basic**.

The letter "p" in pH refers to the "power of 10". The logarithm of a value is the number that, when 10 is raised to it, gives the value. Since $\text{pH}=7$ means that the logarithm is -7 , the value of the concentration must be 0 raised to the -7 (10^{-7}). We can also define the pK_a as $-\log(\text{K}_a)$. Thus, for a conjugate acid/base pair, we have the relationship:

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