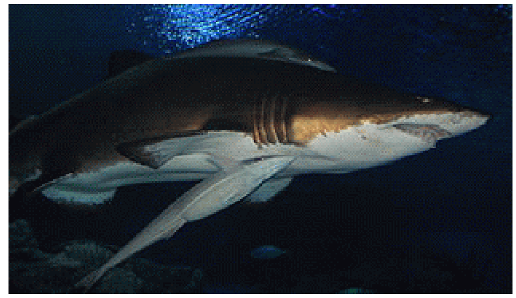
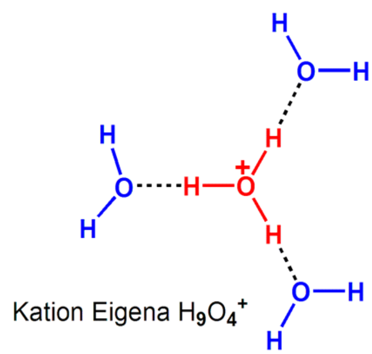
Chapter 7 Acids, Bases and Concentrations

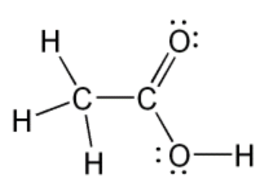


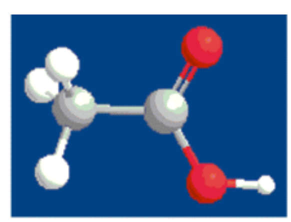
Thoughts or pictures of a shark usually evoke fear. But most sharks are not harmful to humans and shark attacks while dangerous and sometimes fatal are extremely rare. People also often react negatively to the word acid. Much of this reaction is due to a lack of thought or understanding as we encounter acids frequently in our lives. In fact many of us start the day by drinking orange juice, a mixture that contains citric acid. We also commonly put vinegar and oil on our salads but vinegar contains about 5% acetic acid. Our stomachs contain hydrochloric acid to facilitate digestion. However, strong acids used incorrectly can indeed be very corrosive. As part of our introduction to chemistry, we need to gain a better understanding of acids so that we can take advantage of their many valuable uses and avoid hazards from misuse.

Car battery containing sulfuric acid

There are several different definitions acids used by chemists including ones named after Arrhenius, Brönsted and Lewis. For this discussion, the simplest and narrowest Arrheniuis definition that says an acid increases the hydrogen ion content of the solution will suffice. Since a hydrogen atom is simply a proton and an electron (99.98% of hydrogen is the isotope with atomic mass of 1), a hydrogen ion is simply a proton. A proton is a very localized positive charge and will attract and surround itself with any negative charges in the vicinity. Most of our discussion will be confined to using water as the solvent. In water, as a result of the polar hydrogen oxygen bonds, the oxygens have a partial negative charge and orient themselves around the proton. In some books, the symbolism H^+ is understood to represent a hydrated proton. In other books, the H^+ is said to react with a water to form a hydronium ion [$H^+ + H_2O = H_3O^+$]. Still other books combine the proton with several waters to make ions such as $H_9O_4^+$. Here, H^+ will be used to represent protons in water but it should be recognized that the proton is bonded to one or more waters. Using the Arrhenius definition, most acids are written with the proton first such as hydrochloric acid, sulfuric acid and acetic acid: HCl, H_2SO_4 and $HC_2H_3O_2$ ($C_2H_4O_2$). Notice that for acetic acid, hydrogen appears twice in the first formula presented. The reason for this is to distinguish between the two types of hydrogen present. The first hydrogen is bonded to an oxygen with a polar covalent bond. This bond is capable of breaking when acetic acid is dissolved in water as the proton is immediately stabilized by bonding to water. The other three hydrogens are covalently bonded to carbons and do not ionize under virtually any conditions.


Kation Eigena $H_9O_4^+$





The ionization of acetic acid does not go to completion and actually only occurs for only about 1% of the acetic acid molecules introduced into the water.

$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$ (To illustrate the hydration of the proton, this reaction is sometimes written $HC_2H_3O_2 + H_2O = H_3O^+ + C_2H_3O_2^-$)

The extent of ionization is determined by the free energy or the enthalpy and entropy of the reaction. For acetic acid in water, the free energy has a small positive value and reactants are favored over products. When acetic acid is introduced into water, some acetic acid molecules ionize increasing the hydrogen concentration and the acidity of the solution. As soon as some product has been formed, some of the product molecules recombine to form reactants. Eventually, the rate of the forward reaction will equal the rate of the reverse reaction and a state of equilibrium is reached. For acetic acid, the equilibrium favors the reactants and only about 1% are ionized when equilibrium is attained. However, this 1% is very important and significantly affects the acidity of the solution. To understand this better requires that the concept of concentration be introduced.

Different concentration units are in use but chemists prefer the use of molarity. A 1 molar or 1 M solution means that there is 1 mole of the substance in 1 L of solution. It is important to note that the denominator is liters of solution and not liters of solvent. In other words, to make a 1 M solution of sodium chloride, 58.5 grams of sodium chloride (molecular mass of sodium chloride = 58.5 g/mol) is weighed into a flask and diluted to (not with) 1 L with water. Volumetric flasks have been designed just for this purpose. If 1 L of water is added to 58.5 g of NaCl, the volume will come out more than 1 L. Although the volumes are not additive as the NaCl dissociates into Na^+ and Cl^- ions in water and partially fill spaces in the water, the volume of the water does increase with the addition of the NaCl. Thus the resulting molarity will be a little less than 1 if this incorrect procedure is followed. For less concentrated solutions, the error is smaller.


Volumetric flask

As mentioned, acids are very important and useful but can be corrosive. The acid in car batteries, sulfuric acid, is a strong acid and in concentrated form needs to be handled with extreme care. Sulfuric acid can be prepared in any concentration between 0 and 18 M. It is not possible to prepare a solution greater than 18 M as the maximum number of moles of H_2SO_4 that will fit into 1 L is about 18 moles. In the same way, pure water has a maximum concentration of about 55 M as illustrated in the following calculation at 20ºC where the density of water is 0.998 g/mL.

$$\frac{998\text{ g}}{1\text{ L}} \; \frac{1\text{ mol}}{18.0\text{ g}} = 55.4\text{ mol/L}$$

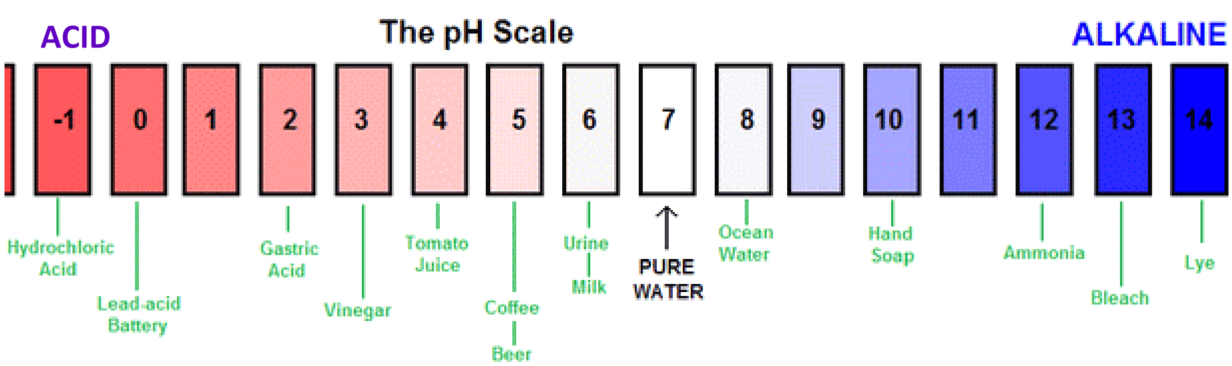
Concentrated or 18 M sulfuric acid is very dangerous and will quickly burn skin. If even a small drop spills on a hand or arm, it needs to be washed off as quickly as possible with a huge volume of water. Vinegar is usually about 5% acetic acid which calculates to about 0.8 M. A 0.8 M solution of sulfuric acid would still be corrosive with a hydrogen ion concentration about 1 M (above 0.8 M because sulfuric acid has two hydrogens per molecule) and must be handled with care. Because acetic acid is a weak acid, the acid concentration is only about 0.004 M. At this concentration of hydrogen ion, the solution is not hazardous and is used on salads. Because it is common for acidic solutions to have low concentrations of hydrogen ion, an alternative scale for communicating acidity has been developed. You have probably heard of the pH scale and perhaps even used it to determine the pH of a pool or of soil.

While compounds described with the word acid in their names clearly increase the hydrogen ion concentration when added to water, even water has some properties characteristic of acids. Water slightly dissociates into hydrogen and hydroxide ions.

$H_2O = H^+ + OH^-$ (or $2\ H_2O = H_3O^+ + OH^-$)

A pure water solution dissociates to the extent that the hydrogen and hydroxide concentrations are 0.0000001 M ($1x10^{-7}$M). This is called a neutral solution and any aqueous solution with a hydrogen ion concentration above this is called at least slightly acidic. pH avoids the use of small decimals by taking the logarithm to the base 10 of the hydrogen ion concentration. In other words p is defined as $-\log_{10}$. Thus pH is $-\log_{10}[H^+]$ and pOH would be $-\log_{10}[OH^-]$. The negative of the logarithm of 0.0000001 M ($1x10^{-7}$M) is 7 which means that neutral water has a pH of 7. Because of the negative sign in the definition of p, any pH values lower than 7 represent acid solutions. Values of pH higher than 7 have hydrogen ion concentrations lower $1x10^{-7}$M and are called basic solutions. Vinegar with a hydrogen ion concentration of about 0.004 M solution would have a pH of about 2.4. It is important to note that because of the logarithmic nature of pH, each change in pH by 1 unit is a 10 fold change in acidity. Also note that the very low concentration of hydrogen ion in pure water, $1x10^{-7}$M, means that tiny amounts of any hydrogen ion donors can significantly affect the pH. One drop of 10 M HCl (approximate concentration of pool acid) added to 1 L of neutral water, will lower the pH from 7 to 3.3. Also note that purified water unless freshly prepared will have a pH of about 6 as a small amount of carbon dioxide from the air dissolves in the water and forms carbonic acid.

$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$ (dissolved CO_2 lowers pH)



While the figure above indicates a pH range of -1 to 14 and some books indicate the range is 1 to 14, the actual range is limited by practical considerations. Since acids are limited to a maximum concentration of about 10 M, the practical lower limit of pH is about -1.

When the hydrogen ion concentration is below $1x10^{-7}$ M and the pH is above 7, the solution is considered to be basic or alkaline. The hydrogen ion concentration is linked to the concentration of hydroxide ion in aqueous solution. When the hydrogen ion concentration is high, the hydroxide is low and vice versa. The relationship can be expressed mathematically by $[H^+][OH^-] = 1x10^{-14}$ or equivalently pH + pOH = 14. When the pH is 7, the hydrogen ion and hydroxide concentrations are equal at $1x10^{-7}$ M and the pOH = 7. When NaOH is added to water, the NaOH dissociates into the ions Na^+ and OH^-. The addition of NaOH to neutral water, raises the hydroxide ion concentration and consequently lowers the hydrogen ion concentration. In addition to the obvious bases that contain hydroxide, many other familiar compounds lead to an increase in hydroxide concentration including sodium bicarbonate, sodium carbonate, trisodium phosphate (TSP) and ammonia. Like strong acids, strong bases are also corrosive and need to be handled with care. Drain cleaning chemicals commonly contain sodium hydroxide which is a strong base. TSP is used for scrubbing walls but also is a strong base. Sodium bicarbonate is an extremely weak base and is safely used in many products including baking powder and antacids.

$NaHCO_3 + H_2O = \mathbf{NaOH} + H_2CO_3$
$Na_2CO_3 + H_2O = \mathbf{NaOH} + NaHCO_3$
$Na_3PO_4 + H_2O = \mathbf{NaOH} + NaH_2PO_4$
$NH_3 + H_2O = \mathbf{OH^-} + NH_4^+$

It is possible to combine an acid (or base) with a salt to form a solution of a required pH that unlike the water example above when a drop of 10 M acid was added, maintains a relatively constant pH when additional acids or base are introduced. These pH change resistant solutions are called buffers and have important roles in the laboratory and in biological systems. For example, your blood is buffered to a pH in the range 7.2 to 7.4. When blood deviates from this range, severe health consequences can result. When people drink orange juice with a pH considerably out of the blood pH range, the buffers in the blood prevent significant pH change making it safe to drink the orange juice.

We observed that some compounds that do not contain hydroxide ions still add hydroxide ions to solutions and can make them basic. There are also compounds that on the surface do not appear to be acids but when dissolved in water, do increase the hydrogen ion concentration and lower the pH. Compounds such as NO_2, SO_2 and SO_3 are in this category. The three products of the reaction are the acids, nitric acid, sulfurous acid and sulfuric acid.

$NO_2 + H_2O = HNO_3$
$SO_2 + H_2O = H_2SO_3$
$SO_3 + H_2O = H_2SO_4$

$C_8H_{18} + 25/2\ O_2 = 8\ CO_2 + 9\ H_2O$

In an internal combustion engine such as the one in most cars, gasoline reacts with oxygen to form carbon dioxide and water with the reaction illustrated for octane above. Air contains 78% nitrogen and 21% oxygen and fortunately, the two gases do not react at room temperature. Inside the engine cylinder, gasoline and air are sparked to cause the explosion of the gasoline. The high temperatures produced are sufficient to cause some nitrogen to react with oxygen to produce nitrogen monoxide.

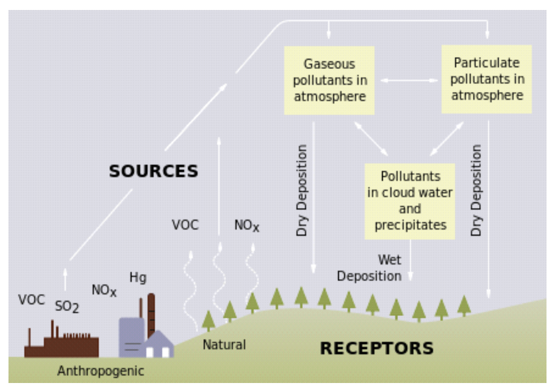
$N_2 + O_2 = 2\,NO$

$2\,NO + O_2 = 2\,NO_2$

The nitrogen monoxide is hopefully eliminated by the catalytic converter but some makes it out the exhaust pipe and is further air oxidized to nitrogen dioxide. Nitrogen dioxide is an orange, toxic gas that is one of the bad constituents of smog. Los Angeles before the requirement of catalytic converters use to be immersed in a cloud of orange smog that could easily be seen when driving over a mountain pass into Southern California. In addition to the smog problem, nitrogen dioxide combines with water in the atmosphere and contributes to the damage caused by acid rain.

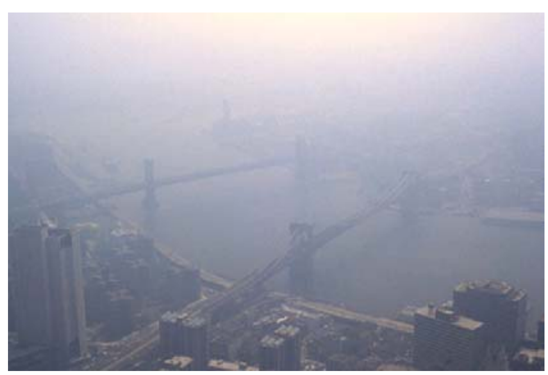
Generation of NO_2

For information on acid rain, please visit:
http://www.epa.gov/acidrain/
http://environment.nationalgeographic.com/environment/global-warming/acid-rain-overview/
http://en.wikipedia.org/wiki/Acid_rain
http://library.thinkquest.org/26026/Environmental_Problems/acid_rain.html
http://ga.water.usgs.gov/edu/acidrain.html
http://geography.about.com/od/globalproblemsandissues/a/acidrain.htm
http://www.berkeyfilters.com/articles/the-causes-and-effects-of-acid-rain-water/



Likewise, coal and oil contain sulfur which upon combustion is converted to sulfur oxides. The sulfur oxides are emitted in the exhaust pipes, combine with water and also contribute to acid rain. The sulfur oxides are partially removed before they can escape and more scrubbing is certainly possible. However, society chooses to balance the environmental damage with economic concerns and in general society is not willing to pay the cost of complete cleanup of the emissions.

The smog and acid rain problems are not the only issues connected with fossil fuel combustion. Later we will look at the effect of the carbon dioxide emissions on climate and the oceans.



Smog over New York City in 1988