

Unit 10: Acids and Bases—The Voyage of the Proton



Unit Overview

Acids and bases result from the movement of a hydrogen ion—a positively-charged single proton, whose electron has been stripped away. The acidity of a solution is based on its concentration of hydrogen ions and is measured on the pH scale. Many reactions must happen in a certain pH range and buffers can help control the pH. This is especially evident in the human body, where the blood acts as a buffer for the many chemical reactions that occur in it. Whether it is manipulating the pH of the soil to control the color of hydrangea flowers or meticulously controlling ingredients to

bake the perfect pastry, acid-base chemistry is all around us.

by Adam Brunet

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Unit 10: Acids and Bases—The Voyage of the Proton

Section 1: Introduction



Figure 10-1. Acids Dissolve Metals

When certain air pollutants react in the atmosphere, they create sulfuric and nitric acids. These substances make rain and snow acidic. The Ulysses S. Grant Memorial in Washington, DC is made of bronze, an alloy of copper and tin; green streaks in this photograph indicate that acid rain is dissolving copper from the statue.

© National Park Service.

In previous Units, we've looked at the properties of solutions, the general properties of chemical reactions, and how their molecules often exist in equilibrium between the products and the reactants. In this Unit, we will be looking specifically at a certain kind of equilibrium reaction that occurs specifically in aqueous solutions. This very important type of reaction involves the release of hydrogen ions by a kind of molecule called an "**acid**."

The behavior of acids and their counterparts, **bases**, is extremely important in much of chemistry. They can act as catalysts for many important reactions, and they are critically important in the study of biochemistry. They are manufactured and sold in large quantities industrially for use in manufacturing many other materials. Some key characteristics of acids, such as their ability to dissolve many metals, can also cause problems. (Figure 10-1)

Glossary

Acid

A compound that has a proton or protons that can dissociate in water; also, when one molecule has a proton or protons that dissociate more readily than those of another (i.e., it has a higher K_a), the first is said to be the *more* acidic molecule.

Base

A compound that has the ability to accept a proton or protons from the surrounding solution. When one molecule associates with a proton or protons from the surrounding solution more readily than another, the first is said to be the *more* basic molecule. A basic compound can also be referred to as "alkaline."

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Section 2: Acids and Bases



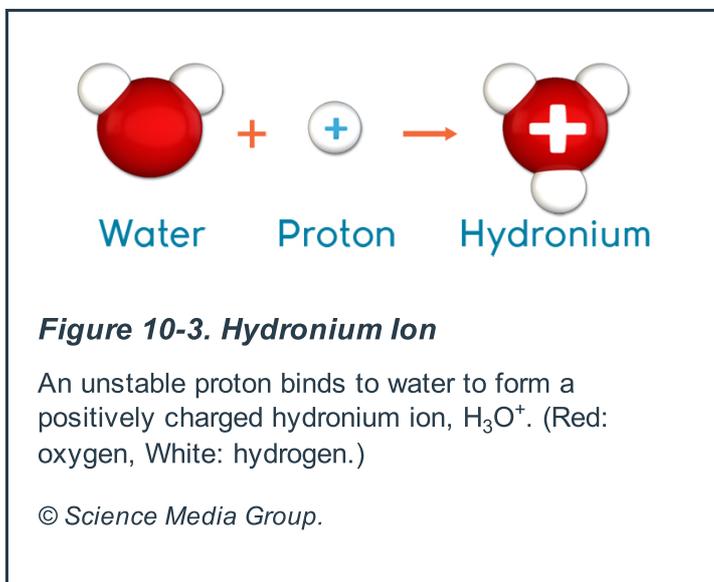
Figure 10-2. Acids

Acids were named from the latin term *acidus*, which means sour. Lemon juice, vinegar, and tomato juice are all acidic solutions, and sour-tasting.

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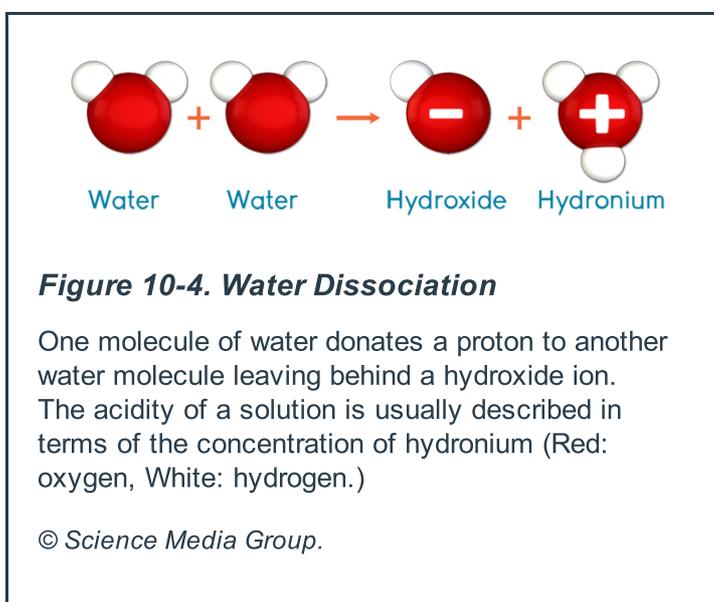
Acids and bases include many familiar substances, such as vinegar (an acid) and baking soda (a base). Acids have a sharp odor and a sour taste (Figure 10-2), while bases often have a bitter taste to humans. However, to better understand what makes a compound an acid rather than a base, we should start with the earliest understanding of acids and base. In 1884, the great Swedish chemist Svante Arrhenius (1859–1927) became the first person to clearly define acids and bases. He said that an acid is a molecule that when dissolved in water produces a proton, or it increases the amount of H^+ ion. Recall, since most atoms of hydrogen have just one proton in the nucleus (without any neutrons) and one electron, a positive hydrogen ion is just a proton. As such, an **Arrhenius acid** is a molecule that when it is dissolved in water, increases the concentration of H^+ ions or can be considered to be a proton donor.

An **Arrhenius base** is a molecule that dissolves in water to produce a **hydroxide ion** (OH⁻) thereby increasing the concentration of hydroxide ions in aqueous solution. One example is lye (NaOH), also known as sodium hydroxide or caustic soda, which is quite dangerous and caustic. Lye is used to make soap, and it is a common component in chemical mixtures used to clean ovens and unclog drains. Sodium hydroxide dissolves into two ions easily in water as shown in the chemical equation here:



Unfortunately, Arrhenius wasn't completely correct in the way he described the chemistry of acids. The problem is a proton is not stable unless it is isolated in a vacuum, and it quickly attaches itself to another molecule. Since nearly all acid-base chemistry is done in aqueous solution, the water molecule is the stable preferred home of the positively-charged proton. So the proton will become associated with an intact water molecule to form what is called a "**hydronium ion**" (H₃O⁺), as shown in Figure 10-3.

It turns out that water all by itself has acid-base properties. In any sample of pure water, a small number of water molecules are always spontaneously forming their own hydronium and hydroxide ions. This process for acids or bases in general is called "**dissociation**". When water dissociates, the protons attach themselves to nearby water molecules to form hydronium. The overall reaction, including both the dissociation of a water molecule and the proton's subsequent association with a second water molecule, is written as below, and illustrated in Figure 10-4. This process is also called the "autoionization of water."



When water dissociates into a hydronium and a hydroxide molecule, the reaction can proceed in both directions. Thus, it is an equilibrium reaction, as discussed in Unit 9. Thus, there is a dynamic balance of water dissociating into hydroxide and hydronium, and hydroxide and hydronium reaction to return to water.

Most molecules in a sample of water do not dissociate. In a liter of water at room temperature, only 0.0000001 moles of water molecules break down, a concentration of 1×10^{-7} M. But some solutions may contain another molecule that also increases the concentration of hydronium ions (H_3O^+), giving these solutions higher proton concentrations than water alone. For example, the proton concentration in a sample of lemon juice is 1×10^{-2} moles per liter (0.01 M) because it contains the molecule citric acid. That means lemon juice has 100,000 times more protons dissolved in it than water has.

Svante Arrhenius (1859-1927)

This Swedish, Nobel Prize winning, chemist was so influential that he even has a lunar crater named in his honor. He established the original definitions of acids and bases and is well known for elucidating the underlying nature of the rate constants in the equations of chemical kinetics. As a child, he was a prodigy, teaching himself to read at age 3 and teaching himself math by watching his father do calculations. He was less impressive to his professors in college where his doctoral dissertation (1884) earned him only a fourth class degree. But the theories on electrolyte conductivity begun in this dissertation were the ones that led to his receiving the Nobel prize in Chemistry in 1903.



Svante Arrhenius. © Wikimedia Commons, Public Domain.

Bases are the counterparts of acids: They accept H^+ protons from water, increasing the concentration of OH^- ions in the solution. Ammonia (NH_3) is a familiar example. When ammonia is added to a solution, it will accept a proton and become an ammonium ion (NH_4^+). This process leaves fewer free protons in the solution than we would see in pure water.

Solutions that have higher concentrations of hydronium ions than water (like lemon juice) are called "**acidic solutions**", and those with lower concentrations (such as ammonia) are called "**basic solutions**." Pure water is right in the middle, not particularly acidic or basic, and we say that the concentration of hydronium ions in water represents a neutral solution.

Glossary

Acidic solutions

Solutions containing a higher concentration of hydronium ion (H_3O^+) than that found in pure water (i.e., having a pH below 7); also, when one solution has a greater concentration of hydronium than another, it is said to be the *more* acidic solution.

Arrhenius acid

Any molecule that can dissociate in an aqueous solution to produce a proton (H^+).

Arrhenius base

Any molecule that can dissociate in an aqueous solution to produce a hydroxide ion (OH^-).

Basic solutions

Solutions containing a lower concentration of hydronium ion than that found in pure water (that is, having a pH above 7). When one solution has a lower concentration of hydronium than another, it is said to be the *more* basic solution.

Dissociation

The process in which a molecule falls apart into two pieces, commonly used to describe when an acid loses a proton (H^+) and becomes its conjugate base.

Hydronium ion

The conjugate acid of water. It consists of a water molecule with an extra proton attached and has the formula H_3O^+ .

Hydroxide ion

The conjugate base of water. It consists of a water molecule with one of the protons abstracted and has the formula OH^- .

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Section 3: The pH Scale

Calculating pH

When describing hydronium concentrations in different solutions we almost always express numbers in scientific notation (e.g., $\text{H}_3\text{O}^+ = 1 \times 10^{-x}$ M or moles/liter). Thus, we create a convention that when we write the pH we just give the absolute value of the exponent, "x," and it is understood that we mean 1×10^{-x} . This was put on a formal footing in 1909 by Søren Peder Lauritz Sørensen (1868–1939), the head of the Carlsberg Laboratory in Denmark, who devised a system in which hydronium concentrations are described in a simple and elegant fashion on a *logarithmic* scale called the "pH scale." The term "pH" is sometimes defined as an abbreviation for "power of hydrogen" to refer to this concentration.

If we take the log base 10 of the hydronium concentration, we just get the exponent, $\log_{10} 10^{-x} = -x$.

But, because the logarithms of $[\text{H}_3\text{O}^+]$ values are all negative for dilute aqueous solutions, Sørensen simplified things even further by dropping the negative sign. With these conventions, a hydronium concentration of 1×10^{-3} is just written as "3." The table below shows some common solutions, their concentrations, and their resulting pH. We can express this mathematically by defining the pH to be the *negative of the logarithm of the hydronium concentration*:

$$\text{pH} = -\log_{10} \text{H}_3\text{O}^+$$

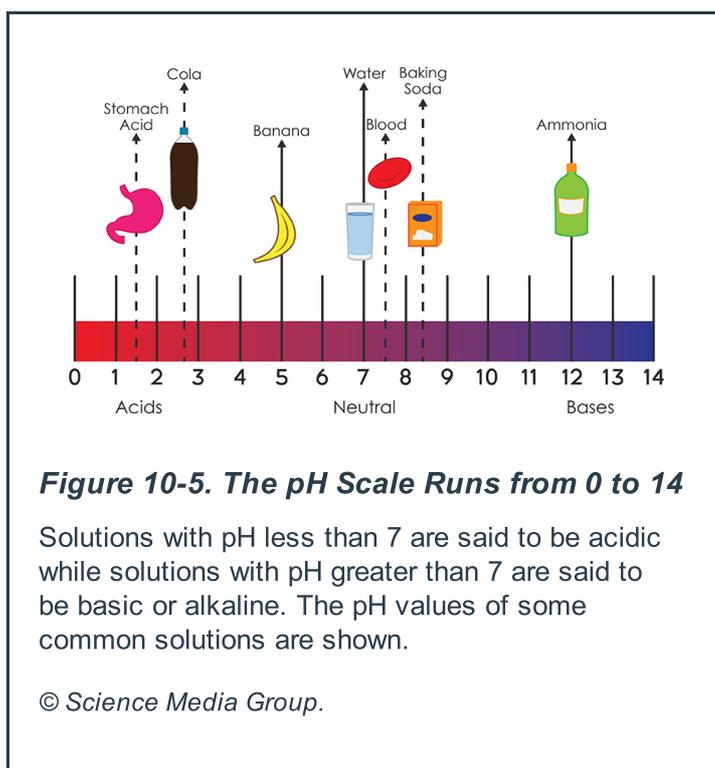
Proton concentrations and pH in common household solutions

Substance	Proton Concentration	Concentration Expressed in Scientific Notation	pH
lemon juice	0.01 moles/liter	1×10^{-2}	2
tomato juice	0.0001 moles/liter	1×10^{-4}	4
maple syrup juice	0.00001 moles/liter	1×10^{-5}	5
water	0.0000001 moles/liter	1×10^{-7}	7
egg whites	0.00000001 moles/liter	1×10^{-8}	8
hand soap	0.0000000001 moles/liter	1×10^{-10}	10
ammonia	0.000000000001 moles/liter	1×10^{-12}	12

Chemists encounter solutions that are acidic and basic all the time, but it isn't necessarily convenient to always give the concentration of H_3O^+ to tell people how much acid or base is in the solution. So, chemists use a scale called the "**pH scale**" for this purpose. On this scale, pure water, which has a concentration of $1 \times 10^{-7} \text{ M H}_3\text{O}^+$ is said to be have a **pH** of 7, which we define as being neutral. This allows for an easy way to say how acidic a solution is. In practice, the hydronium concentration of dilute acidic solutions is almost always expressed as pH and very seldom in molarity. Moreover, the values of pH are actually dimensionless, but are often referred to as "**pH units**." For example, a solution of pH 4.2 and one of pH 5.2 are said to differ by "1 pH unit."

For common solutions we see in a lab or at home, the most acidic solutions and the most basic solutions have pH values that range from about 0 to about 14. In the sidebar, *Calculating pH*, the mathematics behind the pH scale are explained in more detail, but it involves a logarithmic scale, much like the Richter scale used for earthquakes. This means that every pH unit means an increase by a factor of 10. A solution with a pH of 5 contains ten times more acidic protons (H_3O^+) than a solution with a pH of 6. Solutions that have pH values lower than 7 are said to be acidic; solutions that have pH values greater than 7 are said to be basic or alkaline. Figure 10-5 shows the pH values of some common aqueous solutions found in daily life.

One of the things that can be seen in Figure 10-5 is how acidic or how basic a solution is. The more that the pH is below 7, the more free protons or hydronium ions (H_3O^+) are in the solution. The more that the pH is above 7, the more hydroxide ions (OH^-) there are in the solution and it is said to be more basic. As solutions become very acidic or very basic, they also become very dangerous, as they are both highly reactive and corrosive. However, while the solutions can be strongly or weakly acidic (or basic) in terms of it pH, which is measuring those free protons, there is another side to these solutions. The acids and the bases themselves have strengths.



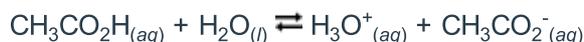
Strengths of Acids and Bases

An aqueous solution that is acidic or basic must contain a molecule in addition to water. Molecules that make the solution acidic by increasing the amount of free protons are called "acids," while those that make a solution basic by binding to the free protons and taking them out of solution are called "bases."

Some acids give up protons more easily than others. Acids that dissociate completely in a solution are called "**strong acids**." For example, this is what hydrochloric acid (HCl) does in water:

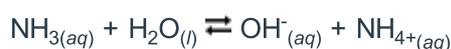


Being completely dissociated means that all or nearly all of the protons on the HCl molecules attached to water molecules increasing the level of the hydronium ions and lowering the pH. However, many acids don't completely dissociate. These acids, such as acetic acid (CH₃CO₂H) are called "**weak acids**." Acetic acid is the main component in vinegar and it undergoes an equilibrium reaction as shown below. In reality, only about a percent of the acetic acid molecules dissociate.



For **strong bases**, it is a little bit different. These are usually metal hydroxides, like sodium hydroxide or lye, which we saw in the last section that just completely dissolve and make a solution rich in hydroxide ions.

But **weak bases** do the same sort of equilibrium reaction that weak acids do. A weak base like ammonia pulls some of the protons off of the nearby water, creating hydroxide ions, but it also is not a complete reaction and only a few percent of the ammonia molecules do this.



It is important to distinguish between acidic or basic molecules, on the one hand, and acidic or basic solutions on the other. When we dissolve a strong acid in water, it will give up all its protons. If the concentration of the molecule is high enough, the resulting solution will be a strongly acidic solution. But if we only dissolve a little of a strong acid in water, there will not be a lot of protons as a result and we will only end up with a weakly acidic solution. For example, with the strong acid, hydrochloric acid, if we dissolve only enough to make a concentration of 1×10^{-6} M the resulting solution has only a pH of 6, and is only a weakly acidic solution.

"Cooking" Fish with Citrus Juice—Ceviche

Ceviche (also spelled cebiche or seviche) is a traditional seafood dish in which fish is marinated in a mixture of citrus juices (like lemon or lime) instead of being cooked. Kinilaw is a similar dish from the Philippines, and there are several such recipes from Polynesia. The acids directly affect the way the proteins in the fish are structured (a process called "denaturing") and makes them look and taste cooked even though no heat was involved.

In general, denaturing is any process that causes the structures of proteins to degrade, or, since proteins are folded up chains, unfold. Heat is the most common way of denaturing proteins, which we see happen when we fry an egg or cook meat. But since proteins themselves have both acidic and basic sections on their surfaces, adding acids to proteins can react with the acids and bases on the surface of the protein molecules, which causes them to change their charge and bonds enough that the proteins unfold. With heat, this process is irreversible, and usually it is with acids.

But one has to be very careful when eating foods like ceviche, because since the food is "cooked" without heat, while the tastes and textures are perfect, the heat often serves to kill any parasites or bacteria that are on the fish.



Ceviche from Peru. © Wikimedia Commons, CC License 3.0. Author: Luis Delboy, 11 July 2008.

On the other hand, if we dissolve a weak acid in water, it only partially dissociates and we will usually only end up with a weakly acidic solution. But if we dissolve enough of even a weak acid, the free protons can build up until we have a strongly acidic solution. For example, acetic acid usually makes only weakly acidic solutions. But, if we add enough acetic acid to water to make solution with a 1 M concentration, its pH will be about 2.4. One hundred percent acetic acid is sold industrially as glacial acetic acid because of the way it forms crystals when it freezes. At this concentration, there are so many dissociated protons that the solution is highly acidic. If it comes in contact with the moisture in our skin it can easily burn us.

The same thing is true for bases, and that's why a household bottle of ammonia has a pH of 12, which is strongly basic, even though ammonia is a weak base. And just to show what happens if things are the same: a 1 molar solution of acetic acid has a pH of 2.4 as seen above. A 1 molar solution of hydrochloric acid has a pH of 0. That is over a hundred times more acidic, even though the concentrations of the acidic molecules are the same. That is the difference between an acid that is strong and an acid that is weak. However, it is important to remember that regardless of the strength of the solution of the acid or base, they can be reactive or even damaging. The *"Cooking" Fish with Citrus Juice—Ceviche* sidebar shows how food can be "cooked" with a solution of a weak acid.

Glossary

PH

A measure of the acidity of a solution. It is the negative log (base 10) of the hydronium concentration in molar ($-\log_{10} [\text{H}_3\text{O}^+]$).

PH scale

A logarithmic scale of the acidity of a solution. For aqueous solutions it runs from -1.7 (most acidic) to 15.7 (most basic), though typical values lie between 0 and 14.

PH unit

One unit on the pH scale. A change of one pH unit in an aqueous solution corresponds to one order of magnitude change in the hydronium concentration.

Strong acids

Acids that dissociate completely in solution.

Strong bases

Bases that completely dissociate in solution, usually soluble metal hydroxides.

Weak acids

Acids that do not completely dissociate in solution.

Weak bases

Bases that do not completely dissociate in solution.

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Section 4: Measuring pH

The Dissociation Constant of Water

In a solution of pure water, some of the molecules spontaneously break down. The dissociation equation for water is shown as an equilibrium reaction.



The mathematical equation that goes with that equilibrium is shown below. It has an equilibrium constant that is called K_w and at 25°C, it has a value of 1.00×10^{-14} . So, in pure water, as it dissociates, it makes an equal amount of hydronium and hydroxide, both at a very dilute concentration of 1.0×10^{-7} M. This is why it is neutral.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

But, because of this equilibrium expression, the concentrations of hydroxide and hydronium always must multiply to give the same value. So, while there is ALWAYS both hydroxide and hydronium in any solution of water, when a solution is acidic, there is more hydronium than hydroxide. And conversely, when a solution is basic, there is more of the hydroxide present. So, measuring the pH, which is just a measure of the concentration of the H_3O^+ ion, also tells us how much hydroxide is present at the same time, because they are both controlled by the K_w equilibrium.

The pH of solutions plays a role in what's going on around you in everyday life. From the water in a swimming pool to the fluids inside our body, the ability to know and control the pH is essential for understanding and controlling these solutions. Therefore, we first need to be able to measure the pH of a solution in order to ensure that our swimming pool is safe or that an industrial process will react efficiently. Nineteenth century biochemists often were frustrated by their inability to get repeatable results from experiments because they had not yet recognized how important it was to control the acidity levels of aqueous solutions. After Arrhenius offered his theories about acids and bases, scientists began to first measure and then control the pH of their experimental solutions, which allowed for many biochemical pathways in the human body to be understood.

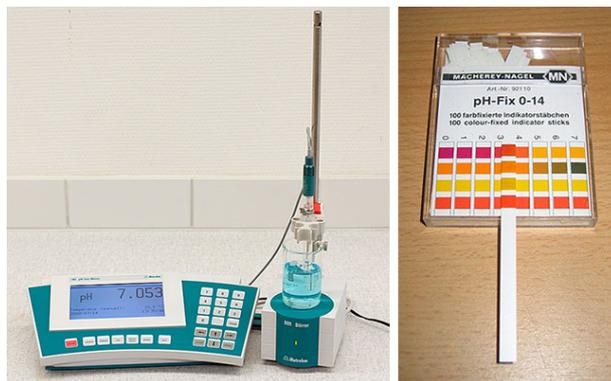


Figure 10-6. pH Meters and Indicators

The most common way to find the pH of a solution is using a pH meter. This can measure the pH with precision of 2 or 3 decimal places. A pH meter has an electrode that can be submerged into a solution to read its pH. Also, there are commercially available pH papers that can be wetted with the solution and then compared to a chart to determine the pH.

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Recall that we have said that a pH of 7 indicates that a solution is neutral. Neutrality does not mean that there isn't any hydronium or hydroxide in a solution, it just means they are present in equal amounts. This is because water, all by itself, dissociates into hydronium ions (H_3O^+) and hydroxide ions (OH^-) as it donates a proton to itself. The sidebar *The Dissociation Constant of Water* explains more about this relationship.

In order to find the pH of a solution, we need to find a direct or indirect way of measuring the concentration of hydronium ions in the solution. This often turns out to be easier than we think because so many processes and molecules are subtly affected by small changes in pH. Using electrochemistry, which will be covered in more depth in Unit 11, the electrode on a pH meter can be submerged in a solution and it will electronically read out the pH of the solution. We can find a pH meter in nearly any chemistry lab. However, pH meters are expensive, so often times indicators are used. An indicator is just a molecule or set of molecules that change color under different pH conditions. These are often impregnated onto strips of paper and called "pH paper." (Figure 10-6)



Figure 10-7. A Natural Color-Changing pH Indicator

Red cabbage juice can be used as a pH indicator. From left to right, the cabbage juice is in a solution with a pH of 1 to a pH of 13. The fourth tube, with the bluish color has a neutral pH of 7. Unfortunately, once the cabbage juice has been exposed to really high or really low pH solutions, it degrades and no longer works as an indicator.

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Indicators

Once scientists discovered the importance of pH, they needed methods for measuring it. Fortunately, many natural materials can be used as pH indicators. For example, red cabbage juice contains a type of molecule called an "anthocyanin," which changes color from bright red when it is mixed in an acidic solution to blue or green when mixed with a base. You can try this for yourself: If you chop up some red cabbage and let it sit in boiling water for fifteen minutes, the resulting solution will change color according to the acidity of what you add to it (Figure 10-7).

Color-changing Flowers

Many other plants also contain various forms of anthocyanins and respond to changing pH differently, so they can be used as indicators in a broad range of solutions of different acidities. Geraniums yield an indicator similar to that found in cabbage, as do rhubarb stems. Hydrangea flowers actually change color depending on the acidity of the soil they're growing in. In acidic soils, the plants can absorb aluminum ions that are present in dirt. The aluminum combines with anthocyanins in hydrangeas' petals to turn the flowers blue. In alkaline (basic) soil, aluminum remains in the dirt, bound to other compounds, so it is not absorbed by the plant, and the anthocyanins in its flowers remain deep pink.



Hydrangeas can indicate the pH of the soil. © Left: Wikimedia Commons, Public Domain. Right: Wikimedia Commons, CC License 3.0. Author: Hectonichus, 29 June 2012.

Some lichens also produce natural pH indicators. One of the oldest indicators that is still in use is Litmus paper—strips of paper soaked in a mixture of chemicals taken from the lichen *Rocella tinctoria* (Figure 10-8). Blue litmus paper turns red when dipped in acid, and red litmus paper turns blue when exposed to base. To this day, people talk about a "litmus test" even in terms of politics when one specific factor is being measured, even if it has nothing to do with pH. For the molecules that serve as indicators, a H^+ ion is added to or removed from the indicator, and that changes the structure of the indicator so that it now absorbs different types of light and appears as a different color. Most indicators just have two possible colors, and there is a specific pH at which that transition occurs. This means that most indicators, like litmus or another one that turns bright pink called "phenolphthalein" can only tell you if a solution is basic or acidic, but not the specific pH. Therefore, there are pH papers and chemicals called "universal indicators," which are actually mixtures of chemicals that change color over a wide range of pH values, and if you have a chart to compare them to, you can then determine the approximate pH of the solution.



Figure 10-8. Litmus Paper

Compounds extracted from the lichen *Roccella tinctoria* (left) can be used to prepare two types of Litmus paper, which are still commonly used in laboratories today. The paper can start off acidic and be red and detect base or the paper can start off blue and detect acid.

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Section 5: Neutralization and Acid-Base Titrations

We know that in a regular glass of pure neutral water there are small amounts of hydronium (H_3O^+) and hydroxide (OH^-) ions, but they are equal in number and balance each other and we say that the solution is neutral or has a pH of 7. However, what happens when large amounts of hydronium ions and hydroxide ions are combined together by mixing an acidic solution with a basic solution?

Acid Rain

That rain is often acidic was first noted in the nineteenth century, but not until the twentieth century did that acidity become widespread at the dangerous levels we associate with the term "acid rain". In the 1970s, it was determined that the cause of the increasing acidity of rain was due to release of industrial pollutants to the atmosphere, often quite far away from the area where the rain was falling.

The principle culprit turned out to be coal, which contains sulfur as an impurity. When burned in a power plant, this sulfur combines with oxygen to form sulfur dioxide which is lofted up through the smokestack and disperses through the atmosphere. Once in the atmosphere, it undergoes a series of further reactions, which culminate in the formation H_2SO_4 —sulfuric acid.

Sulfuric acid is a very strong acid, and when water condenses out of the air to form rain drops, the acid is dissolved in the water. The rain then falls and collects in bodies of fresh water, raising their acidity. The northeastern United States has suffered the most from this, because the Ohio Valley, including areas of Ohio and Pennsylvania, are the locations with most of the coal-based industry of the last century and a half. Due to prevailing weather patterns, these smokestack gases enter the atmosphere in the Ohio valley, but rain down upon upstate New York and New England.



Trees damaged by acid rain. © Wikimedia Commons, Public Domain.

The increase in the acidity of rain can have devastating consequences. Metal impurities in the soil that are normally tightly bound to other compounds can be washed by acidic rain into lakes and streams; at one time many ponds in New England were found to be unable to support brook trout because of this. Plants are also highly sensitive to soil pH. Beneficial nutrients may also be washed out of the soil, leaving plants unable to survive in it. In particularly hard-hit areas, scores of dead trees can be found, like those shown above.

Buildings and statues have also been damaged by acid rain, which eats away at stone, especially limestone. The increased erosion of statuary, gravestones, and even some buildings has resulted in tremendous loss—some works of art have been completely destroyed.

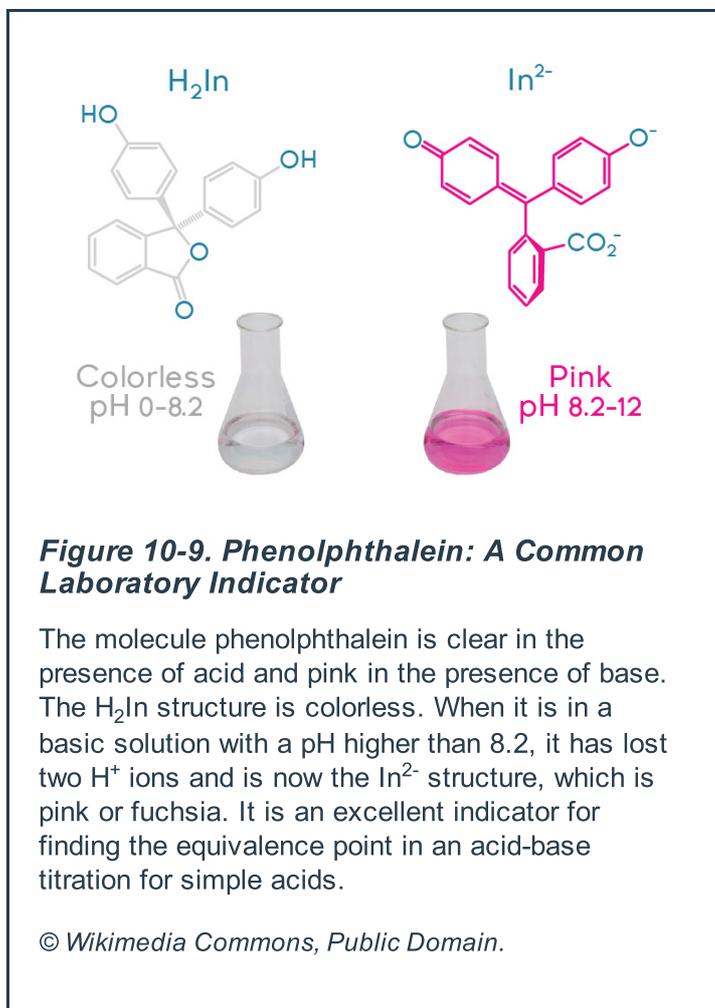
Starting in the late 1980s, the Environmental Protection Agency (EPA) instituted a program to curb the emissions of sulfur dioxide and other pollutants that cause acid rain. Since then, emissions have been reduced a great deal and the resulting acid rain has therefore also declined. The problem is far from eliminated, however, and much remains to be done about this serious environmental challenge.

Let's consider hydrochloric acid (HCl) which is the major component of stomach acid, and sodium hydroxide (NaOH) which is often referred to as "lye," and is used in soap-making. When dissolving a strong acid like hydrochloric acid in water along with a strong base like sodium hydroxide, at first it produces hydronium ions (H_3O^+) and chloride (Cl^-) ions from the dissociation of HCl, along with hydroxide (OH^-) and sodium ions (Na^+) from the dissociation of NaOH. But nearly all of the hydronium and hydroxide combine to make water molecules, leaving behind only spectator chloride and sodium ions. If the amount of hydrochloric acid is exactly the same as the amount of sodium hydroxide, in moles, then each hydronium should have a hydroxide to react with leaving behind a solution that is now neutral. In theory, it should be a glass of just pure water now, with a pH of 7 and normal table salt (NaCl) dissolved in it. We start with two extremely caustic substances and end up with benign products.

In general, when acids and bases react together, they neutralize each other and the pH of the solution gets closer to 7. This is called a "**neutralization reaction**." Only when an equal amount of a strong acid and a strong base are added together is the pH going to be exactly 7. But many times, weak acids and weak

bases are combining. Still, the pH will get closer to 7 but the solution won't be neutral. In the case of acid rain, the rocks and soil are often basic, especially carbonate rocks found in certain parts of the country. As the weak acids in acid rain fall on the rock, they are neutralized by the bases on the leaves, in the dirt and in the rocks. However, many of these bases, such as those in the rocks, are non-renewable. Once a century of acid rain falling on the rocks has neutralized all the base in the rocks, the acid rain just enters the ecosystem with nothing to neutralize it.

Titration



In Section 5 of Unit 8, titrations were introduced as a way of combining two solutions together to have a controlled stoichiometric reaction take place. It requires having a solution of a known concentration, usually in a burette, that will react with a solution of an unknown concentration in a beaker below it. Any reaction will work for a titration, but to be able to tell when the reaction is done, there must be a visible endpoint. For acid-base reactions, indicators can provide just this type of information with a color change to indicate the endpoint. Therefore, acid-base neutralization reactions are one of the most common types of reactions used in titration analyses. Thus, a titration can be used to determine the amount of acid or base in an unknown solution.

When titrating strong acids with strong bases, the endpoint is reached when the pH will be exactly 7 because the solution should just be a pure water solution with neutral electrolytes in it. Once the acid is gone, any more base we add to the flask will not be neutralized, and the solution's pH will start to rise. However, even a small fraction of a drop from the burette of excess strong base will move the pH up a unit or two. We use an indicator to detect the point at which this happens. One such indicator, phenolphthalein ($C_20H_{14}O_4$), is clear and colorless in acidic solutions but turns deep pink in basic solutions if the pH is higher than 8.2 (Figure 10-9). The fact that phenolphthalein changes color a little above 7.0 usually leads to only very small error in the experiment.



Figure 10-10. Acid-base Indicators Come In Many Types.

In addition to phenolphthalein, other indicators include bromothymol blue and methyl orange. For solutions that are just only slightly basic at their endpoint, bromothymol blue is a good indicator. Just below a pH of seven, the solution has a yellow color that becomes blue just above a pH of 7. When the endpoint of a titration is going to be rather acidic, methyl orange is used. Methyl orange does not have a sharp transition, but undergoes a change from pink-red to yellow-orange around pH 3.5.

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However, when titrating a base with an acid, one would want an indicator that changes color just a little bit below 7. And what happens when titrations involve a strong acid or base being added to a weak acid or base? In that case, the pH at the end point might be higher or lower than 7 and one must choose an appropriate indicator that changes color in the right pH range. Two commonly used indicators include bromothymol blue and methyl orange, and there are many others. Usually, bromothymol blue is useful when you expect the endpoint to have a pH almost exactly near 7, and methyl orange is ideal when the pH at the endpoint is weakly acidic. Figure 10-10 shows the two colors that each of these indicators switch between.

Glossary

Neutralization reaction

A reaction in which an equal amount of an acid and a base are mixed together, cancelling each other out, and making the solution neutral with a pH of 7.

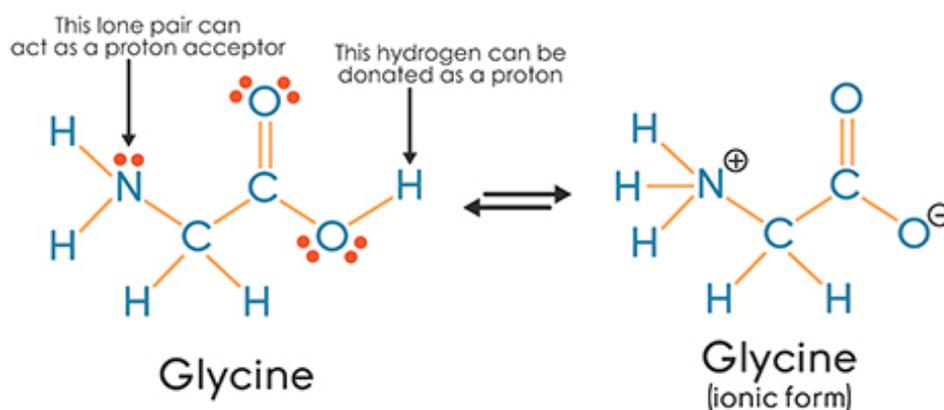
Unit 10: Acids and Bases—The Voyage of the Proton

Section 6: Conjugates of Acids and Bases

Arrhenius provided the first definitions of acids and bases, but in 1923 Danish chemist Johannes Nicolaus Brønsted (1879–1947) and English chemist Thomas Martin Lowry (18747–1936) took this field to a new level. Their individual discoveries led to a new concept of Brønsted-Lowry Acids and Bases. According to their definition, a **Brønsted-Lowry acid** is anything which can donate a proton (H^+) and a **Brønsted-Lowry base** is anything that can accept a proton.

Amphoteric Compounds

When acetic acid is added to water, the water was considered the base. However, when ammonia is added to water, the water is the acid in that reaction. There are some molecules that can behave as an acid or as a base depending on the situation and the other acids and bases present. These molecules are called "amphoteric compounds." This term uses the amph-prefix, which comes from the root for "both" like with amphibians who live on both land and in the water. Another example of amphoteric compounds are the proteins found in living things that are made up of strings of amino acids linked together in a chain. There are many types of amino acids, but they all have a nitrogen with a lone pair that can act as a proton acceptor, and a proton attached to an oxygen that can be readily donated. An example of this is shown below for the amino acid glycine.

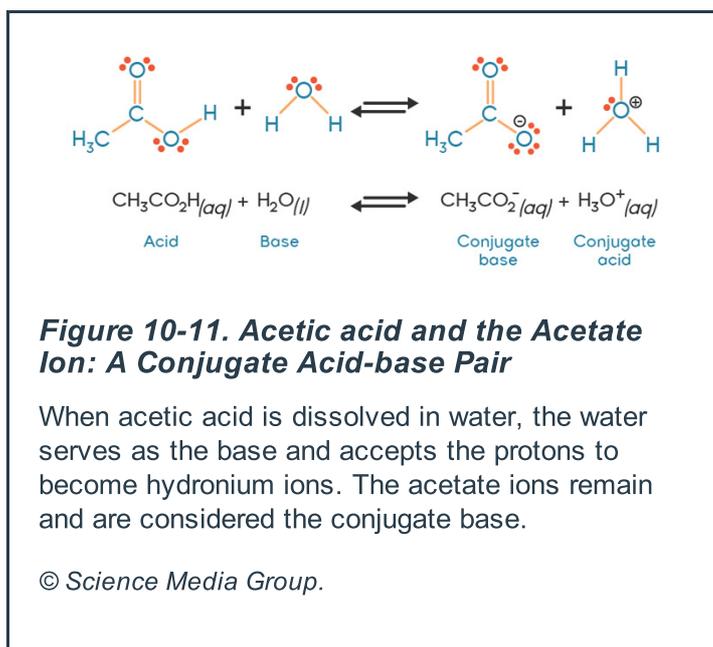


Glycine molecule and its ionic form. © Science Media Group.

Not all amphoteric compounds have a form that contains both a positive and negative charge at the same time, but the amino acids all do. This ionic form is called a "zwitterion" from the German word *zwitter*, meaning "hybrid."

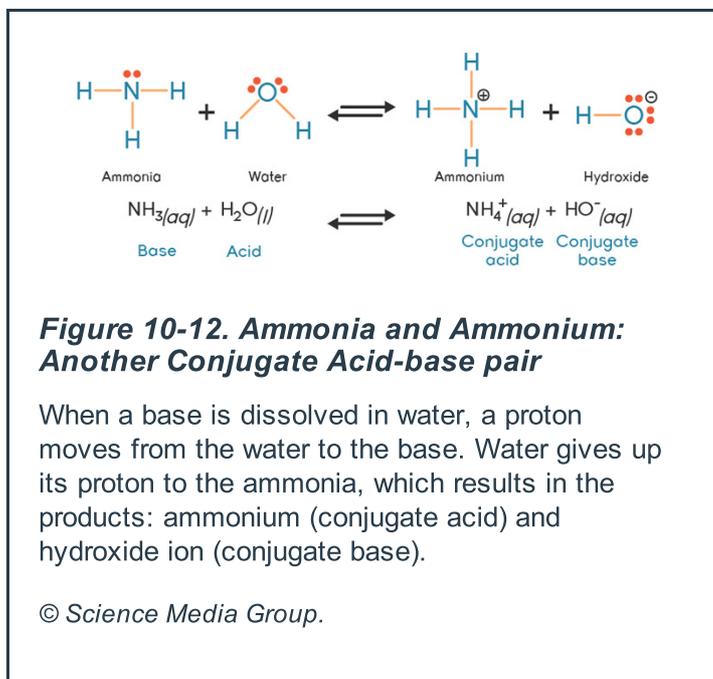
Brønsted and Lowry saw that hydroxide ions were not the only substance that could decrease acidity; in the Arrhenius definition of a base, only a hydroxide salt that dissolved into hydroxide ions and raised the hydroxide concentration directly was considered to be a base. With this newer definition, any molecule would be a base if it could lower the concentration of hydronium ions in a solution to which it was added, either by pulling a proton off of a hydronium ion to leave a water molecule or by pulling a proton directly off of water to make a hydroxide ion.

This new definition of acids and bases focuses much more on this proton (H^+) that is moving around in the solution. So much so now that we change how we talk about acids and bases when we have a written out acid-base reaction. To understand this, first let's focus on the behavior of the weak acid, acetic acid, as it interacts with the water.



Many molecules are acidic; they have a proton that can come off, so they exist in two forms—one with the proton attached and the other without it. We defined a Brønsted-Lowry acid as a molecule that can donate a proton. The form of the molecule that has the proton still attached to it is the acid form. A Brønsted-Lowry base is a molecule that can receive a proton, so the form of the molecule that is lacking the proton is the basic form, since it is ready to receive and bind to a proton.

Perspective is everything. Sometimes we are looking at a molecule in its acidic form, and we want to refer to the molecule as it will be after it has given up its proton. When the proton is dissociated, the remaining molecule is then called the "**conjugate base**" of the acid. On the other hand, if we are looking at a molecule without a proton and we want to refer to the form it will have after it has picked up a proton, we call that protonated form the "**conjugate acid**" of the base. In our example with acetic acid as shown in Figure 10-11, the water served as the base to accept the proton from the acetic acid, which turned the water into the hydronium ion, which is the conjugate acid of water. The key in Brønsted-Lowry acid-base chemistry is that acids and bases always occur as a pair with their conjugate. So, acetic acid and the acetate ion form a conjugate acid-base pair. This will be essential for understanding the strengths of acids and bases later in this unit.



When a base is dissolved in water, once again a proton moves from the acid to the base. In Figure 10-12, we see the ammonia molecule (NH_3) has a lone pair on its nitrogen that can bind to a proton to make an ammonium molecule (NH_4). In this case, the water is serving as the acid, giving up its proton to the ammonium, and becoming the hydroxide ion, the conjugate base of water.

Molecules besides ammonia that contain a nitrogen atom are called "amines," and they can pick up a proton from water just like ammonia. Such compounds are thus basic like ammonia. Amine bases are very common in biochemistry. The four types of nucleotides that encode the information in our DNA—adenine, cytosine, guanine, and thymine—are amine bases.

Glossary

Brønsted-Lowry acid

A molecule that can dissociate in an aqueous solution to produce a proton, thus increasing the concentration of hydronium ion in the solution.

Brønsted-Lowry base

A molecule that can pick up a proton from aqueous solution, thus decreasing the concentration of hydronium ion in the solution.

Conjugate acid

The form of a molecule that has a dissociable proton attached to it. Since that proton can dissociate, this molecule is an acid.

Conjugate base

The form of a molecule that has a proton dissociated from it. Since that proton could potentially re-associate with the molecule, it is said to be a base.

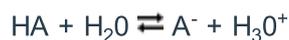
Unit 10: Acids and Bases—The Voyage of the Proton

Section 7: The Strength of Acids and Bases—The Acid Dissociation Constant, K_a

Imagine that we have dissolved some generic acid, HA, in a flask; after a few moments an equilibrium will be established with some of the HA dissociated. Depending on if the acid is strong or weak, there could be almost no HA left undissociated. There will be some concentration of hydronium (H_3O^+), some concentration of the conjugate base (A^-), and some remaining concentration of the acid (HA). However, how can we use this equilibrium to our advantage to understand if our acid is strong or weak, so that we can be able to compare them to each other? One way to do this requires us to combine these equilibrium concentrations into an equilibrium constant, which is discussed in Unit 9.

The equation for the dissociation of any acid can be written in a generic form, as shown below. When we write the equivalent equation for a specific acid, it is called the "**acid dissociation equation**" for that acid. There is an equilibrium constant for that acid reaction which is called the "**acid dissociation constant**," or K_a .

Generic Acid Dissociation Equation



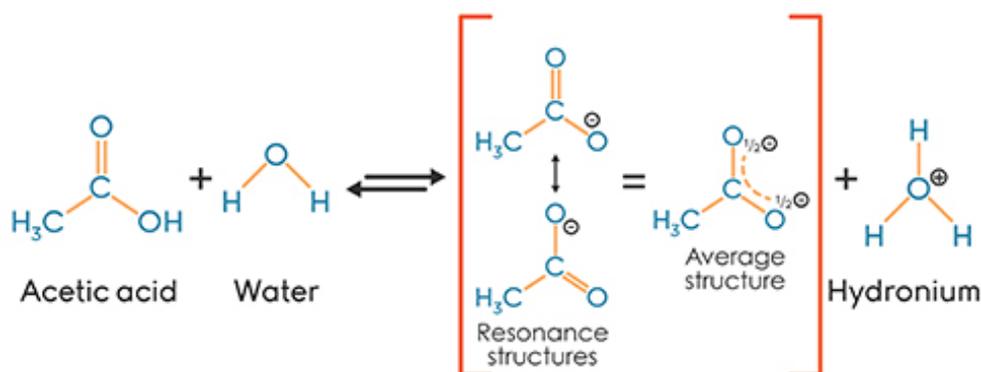
Corresponding acid dissociation constant

$$K_a = \frac{[A^-] [H_3O^+]}{[HA]}$$

Resonance and Acidity

In Unit 5, we looked at the phenomenon of resonance, in which a single molecule can have its electrons arranged in several ways. We saw that the molecule behaves as though it were an *average* of all the different electron arrangements. When the placement of electrons is averaged out this way, it can affect the stability and acidity of the molecule.

For example, consider the acidities of ethanol and acetic acid, shown below. They differ by the addition of an oxygen double bond on the second carbon in the acetic acid, and this difference affects the stability of the conjugate base of these molecules.



Molecules with resonance, like acetic acid, are more acidic than molecules that do not exhibit resonance, like ethanol. © Science Media Group.

An ethanol molecule is not an acid. This is because when $\text{CH}_3\text{CH}_2\text{OH}$ loses a proton it becomes $\text{CH}_3\text{CH}_2\text{O}^-$, which is an anion that is not particularly stable, and it has no resonance structures. However, with acetic acid, once it loses a proton, it forms an acetate ion, and the acetate ion has two different resonance structures. This means the two oxygens share half of a negative charge on them, rather than the full -1 charge on the oxygen in ethanol. So, if an anion is more stable and able to hold its negative charge, then it is less likely to want its proton back, which makes it more acidic. Thus, in general, molecules that exhibit resonance after losing a proton are more acidic than similar molecules that do not.

Molecules that have a carbon double bonded to an oxygen and also bonded to an OH group—like acetic acid—are called "carboxylic acids." Any molecule like this can form resonance structures like those shown above, and consequently can give up its proton easily. They are all at least mildly acidic. Carboxylic acids are very common in organic chemistry and biochemistry and the vast majority of the acids in the body are some form of carboxylic acid.

It turns out that if we know the concentration of an acidic solution and the K_a for the acid, we can calculate the pH from those values. Or, if we have a pH meter and we know the concentration of an acid in solution, we can calculate what its K_a must be. What this means is that the concentration of an acidic solution, its pH and the K_a of the acid are linked together by the acid dissociation equilibrium so that if we know any two of those three values, we can find the third.

Acid Strength and K_a

If the molecule HA is a strong acid the concentrations of the products H_3O^+ and A^- will be much greater than the concentration of the reactants, water and the undissociated molecule, HA. We describe this by saying the equilibrium "lies to the right." In this case, the acid dissociation constant (K_a) will be quite large. Strong acids have large values of K_a , which means that they are greater than 1. Conversely, for weak acids

a smaller fraction of the molecules are dissociated, so the concentration of HA will be larger relative to that of H_3O^+ and A^- ; we would say the equilibrium in this case "lies to the left" and the value of K_a will be small, or usually much smaller than 1. The acid dissociation constant, then, is a measure of how acidic a particular molecule is: The larger the K_a , the stronger the acid.

pK_a

The K_a of an acid tells us how likely that acid is to give up a proton when it's in an aqueous solution. Table 10-1 shows the values of K_a for a variety of acids. However, K_a values are relatively small and hard to use and compare, so chemists have created a related value called the " **pK_a** ." Just as with pH, pK_a is a notation or shorthand that lets us work more easily with tiny numbers, because the $pK_a = -\log_{10}K_a$. The pK_a values for a variety of acids are also shown in Table 10-1 alongside the K_a values to which they correspond. Since the dissociation constant is a set number for a particular type of acid, pK_a is a property of the molecule. This is in contrast to pH, which expresses the concentration of aqueous hydronium ions and so is a property of the solution. For example, a 1×10^{-2} M solution of acetic acid has a pH of 3.4, while a 1×10^{-4} M solution of acetic acid has a pH of 4.5. In both solutions, however, the pK_a of the acetic acid molecules remains 4.76.

Table 10-1. K_a and pK_a Values For A Variety Of Acids

Acid	K_a	pK_a
ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)	1.8×10^{-16}	15.7
phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.12×10^{-10}	9.95
acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)	1.74×10^{-5}	4.76
hydrofluoric acid (HF)	6.31×10^{-4}	3.2
hydrochloric acid (HCl)	1×10^7	-7

We said earlier that K_a is a measure of how strong an acid is. Usually the equilibrium constants are expressed using pK_a , and as values for K_a increase, the corresponding values of pK_a decrease. Thus, the smaller the value of a molecule's pK_a , the more acidic that molecule is. Weak acids have pK_a values between 0 and 15.5. Strong acids have negative pK_a values that are below zero, and compounds that have pK_a values that are over 14 are considered to be neutral compounds (non-acids) when dissolved in water.

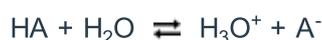
Glossary

Acid dissociation constant

A form of the equilibrium constant for the dissociation of an acidic molecule into a proton and its conjugate base. It is abbreviated " K_a ." The acid dissociation serves as a measure of how acidic the molecule is; the larger the value of K_a , the more acidic the molecule.

Acid dissociation equation

The chemical equation for the separation of an acidic molecule into a proton and its conjugate base. The general form can be written:



where HA is the acidic molecule, H_3O^+ is the stable form of the proton, and A^- is the conjugate base of the acidic molecule.

pK_a

A measure of the ease with which the proton dissociates from an acidic molecule. It is equal to the negative log (base 10) of the acid dissociation constant ($-\log_{10}K_a$).

Unit 10: Acids and Bases—The Voyage of the Proton

Section 8: Conjugate Acid-Base Strengths

Now we have a system of using pK_a values to express if acids are strong or weak, and just how strong and weak they are. However, we have also seen that every acid has a conjugate. It turns out that these same pK_a values can help us understand the acid-base properties of its conjugate as well.

In a similar way to acids, the general base equation is also an equilibrium:



Because the proton and the base (B) are coming together, rather than splitting apart, this should properly be called the "base association constant" (K_b). Generally, this value is small and so is expressed as pK_b , using the notation discussed for pK_a :

$$pK_b = -\log_{10}K_b$$

If, for some particular base, the above base association equation lies to the right, that base has a strong tendency to pick up protons from the water in the environment. The value of K_b will be large, pK_b will be small, and we will refer to the molecule as being a relatively strong base. If the equilibrium lies to the left, the molecule has only a small tendency to accept a proton; hence the value of K_b will be small, pK_b will be large, and we will refer to the molecule as being a weak base. Just as it was with acids, the smaller the value of a molecule's pK_b , the more basic it is.

What this means is from a Brønsted-Lowry perspective, if you have an acid (HA), it also has a conjugate base form (A^-). For a generic base (B), its conjugate acid BH^+ could act as a proton donor. So, how can we compare this conjugate pair when we only know about the pK_a of the acid or the pK_b of the base? It turns out, that in water at 25°C, the pK_a and the pK_b values always add up to 14, for a conjugate acid-base pair. So if we have a generic conjugate of an acid A^- and we dissolve it in water we have this equilibrium below, which has a K_b or K_b associated with it.



So, let's say we have sodium acetate (NaCH_3CO_2), which contains the neutral sodium spectator ion and the acetate ion, which is the conjugate base of acetic acid with a pK_a of 4.76. Using the above relationship, we can see that if they must add up to 14, the pK_b for the acetate ion is 9.24, which means that it is a weak base!

Since this relationship is always true, we can say something even more powerful: A weak acid has a weak conjugate base, and conversely, a weak base has a weak conjugate acid. This can be seen with the HCN example in Table 10-2.

Table 10-2. Relationship Between pK_a And pK_b

Acid	pK_a	Conjugate Base	pK_b
Hydrochloric acid (a strong acid), HCl	-7	Chloride ion (a neutral ion), Cl^-	21
Hydrogen cyanide (a weak acid), HCN	9.3	Cyanide (a weak base), CN^-	4.7
Water (neutral compound), H_2O	15.7	Hydroxide (a strong base), OH^-	-1.7

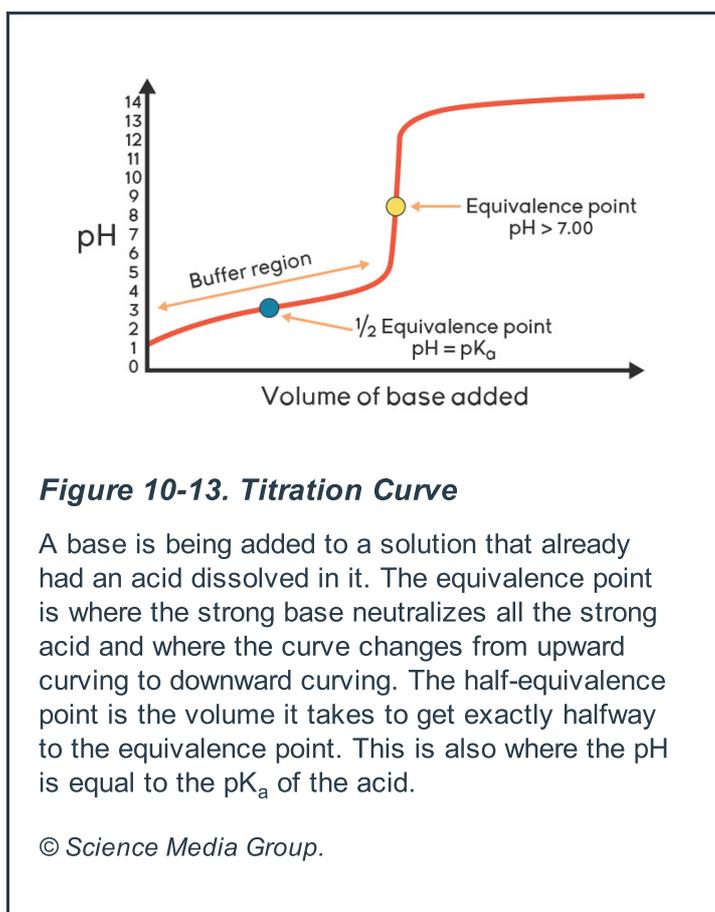
This has other implications. It means that if we have a strong acid, with a pK_a less than zero, its conjugate base is going to have a very high pK_b value, too high to behave as an acid. Therefore, in general, the conjugate of a strong acid or a strong base will be a neutral conjugate.

Unit 10: Acids and Bases—The Voyage of the Proton

Section 9: Titration Curves

Titration (see Section 5 of this unit) is a method commonly used to analyze a solution in order to determine the amount of acid in it using stoichiometry. However, there is another form of titration too, in which we titrate a weak acid with a strong base, or conversely we can titrate a weak base with a strong acid. While in this titration, we can still detect the end point or the **equivalence point**, the important part is that as we add the strong base drop-by-drop into the solution of the weak acid, we constantly measure the pH of the solution so we can create a graph called a "**titration curve**."

Some things we can imagine even before looking at a titration curve, like that shown in Figure 10-13. For example, if we're titrating a weak acid, the pH should start off below 7, and it should rise as we add base to it. Since we're adding a strong base to a weak acid, it completely neutralizes all the weak acid it runs into, which leaves a mixture of weak acid and its weak conjugate base. This will continue on until we have added exactly enough strong base to neutralize all the strong acid, which happens at the equivalence point, and at that point only the weak conjugate base is left in the solution, so the pH should be greater than 7.



If we keep adding more strong base, the solution's pH will rise quickly again. It turns out as we approach and leave this equivalence point, the pH rises very quickly, and the titration curve goes from being upward curving to downward curving. The point where the curve changes, which way it curves IS the equivalence point. So, this means we don't even need an indicator to see when an acid-base titration has reached equivalence: all we have to do is look for the middle of the steepest part of the graph and that's where the curvature of the curve changes.

There is one other reason people use a titration curve instead of using a pH indicator to find the equivalence point in a titration. This is because there is one other very important piece of information about the acid within the shape of this curve. First, if we look at the titration curve, we'll see that between where it starts and the equivalence point, it continues to rise, but rather slowly. This section is called the "buffer region". (The next section will discuss what a buffer is.) However, in the middle of the buffer region is another special point on the titration curve called the "half-equivalence point." This is the volume it takes to get exactly halfway to the equivalence point, which we cannot actually determine until after we have found the equivalence point. This point can be found by taking the volume at the equivalence point and dividing it by two. Why do we care about this point? This is because the pH at the half equivalence point is equal to the pK_a for the acid. This provides chemists with an easy tool to determine the pK_a for an acid by just doing a titration with a pH meter and creating a titration curve.

Glossary

Equivalence point

The point in a titration when the number of moles of added reactant is exactly equal (or stoichiometrically proportional) to the number of moles of reactant in the sample.

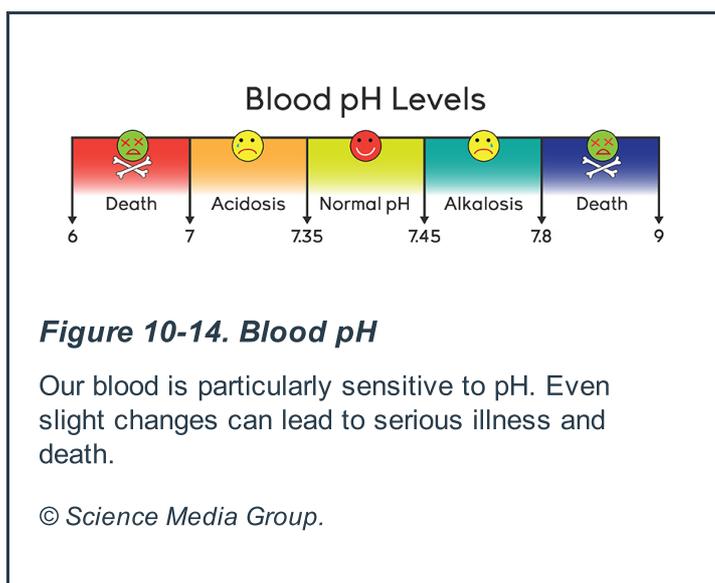
Titration curve

A graph with the pH of an acidic or basic solution (being tested) as the dependent variable vs. the amount of added acid or base as the independent variable. The rate of change in pH can be used to determine the equivalence point.

Unit 10: Acids and Bases—The Voyage of the Proton

Section 10: Buffers

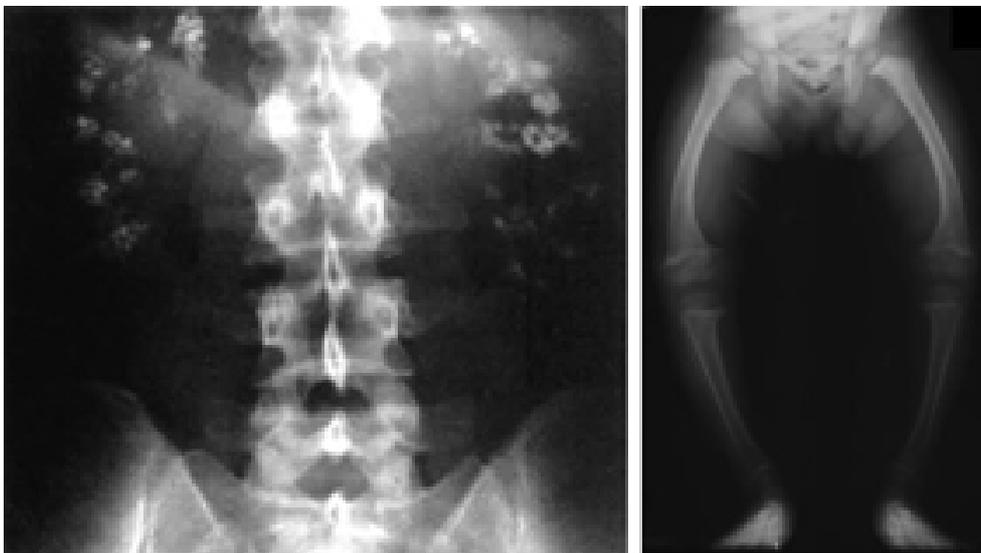
Biochemical reactions are particularly sensitive to the pH of the solution in which they occur. Blood circulating within the human body has a natural pH of 7.4. Changes of half of a pH unit in either direction (below 6.9 or above 7.9) for a long enough time can cause severe illness or death (Figure 10-14). So, what do biological systems do to control this pH? The answer is they use **buffers**.



Many chemical reactions are highly dependent on pH; it is therefore often useful to carry them out under conditions in which the pH maintains a stable value as the reactions occur. This can be achieved by preparing a buffered solution. Buffered solutions, or simply buffers, have the property that when an acid or base is added to them, their pH changes very little. How can this be? To answer this question we need to examine the components of a buffer in more detail.

Acidosis and the Body

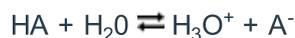
The pH of the blood is carefully regulated by the body. It must remain right around 7.4 or serious damage results. The kidneys play a large role in maintaining the ideal pH by removing acid from the body and excreting it in the urine. When this process goes awry, blood pH starts to change with dramatic consequences ranging from calcifications in the kidneys to bone problems like rickets and the bowing of the legs.



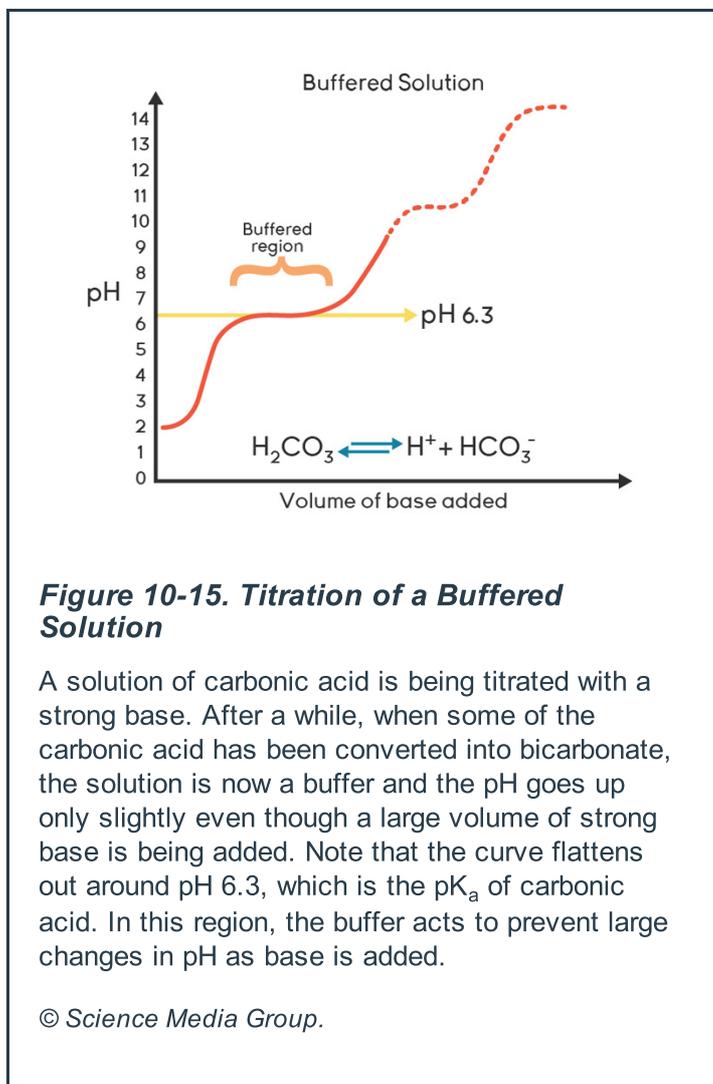
Effects of altered pH on the body range from calcifications in the kidneys to bowed legs. © Left: Wikimedia Commons, Public Domain. Right: Wikimedia Commons, CC License 1.0. Author: Mrich, 28 September 2004.

A buffer is most easily prepared by dissolving *an acid together with its conjugate base* in the same solution. The precise acid and conjugate base used is said to constitute a particular **buffer system**. For example, the buffer system composed of carbonic acid (H_2CO_3) and its conjugate base bicarbonate (HCO_3^-) is one of the mechanisms by which the human body maintains a steady pH in the bloodstream. It turns out that any mixture of weak acids and weak bases will serve as a buffer, and human blood has dozens of compounds in it that are weakly acidic or weakly basic, including carbonates, phosphates, and proteins.

The reason buffers work is because there is an equilibrium between the acid and its conjugate base:



If we add some stronger acid to the solution, it will donate its protons to the A^- and convert some of them into HA. As long as there are both reasonable amounts of HA and A^- in the solution, it stays in the buffer region and the pH changes only slightly up. All that happened was the equilibrium above was shifted a little bit according to Le Chatelier's Principle. By comparison, if the solution were not buffered, every proton released by the strong acid would exist as a hydronium ion, and the pH would change considerably.



But, instead of an acid, what if we add a strong base to the buffered solution? It will steal some of the protons off of the HA in the solution and it will form some conjugate A^- as a result. Once again, as long as there are still reasonable amounts of HA and A^- still in the solution, it will still be a buffer and the pH will have gone up only slightly.

The ability of a buffer system to flatten out changes in pH is strongest when the value of the solution pH is near the pK_a of the acid in the buffer system. The pK_a of carbonic acid is 6.3; consequently the buffering capacity of a carbonic acid/bicarbonate buffer system is greatest around this value (Figure 10-15). We would choose this buffer system if we wanted a solution to stay near a pH of 6.3. Also, note that once too much base has been added, and the solution is no longer a mixture of weak acid and weak base, the pH begins to rise quickly again as it is no longer a buffer.

Glossary

Buffer

An aqueous solution having the property that its pH changes very little upon the addition of an acid or a base. A buffer is formed by mixing together combinations of weak acids and weak bases.

Buffer system

A weak acid and the salt of its conjugate base, which together can be used to create a buffered solution.

Unit 10: Acids and Bases—The Voyage of the Proton

Section 11: Conclusion

This concludes our look at the central concepts of acids and bases. When dealing with aqueous solutions, it is always important to understand the role acids and bases are playing, and to control for the pH levels. This is especially important when running reactions to synthesize materials in the lab, and it holds true for when the cells of our bodies are synthesizing molecules as well.



Figure 10-16. Cottage cheese and pH

When milk goes bad, bacteria growing in it give off acidic waste products; when acid is added to milk, its pH decreases. When the pH of milk goes down, the protein in it (known as casein) falls out of solution as white curds—cottage cheese.

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Acidity is a factor that helps to produce many familiar products. Cottage cheese is one interesting example. As milk sours, part of it is slowly converted into lactic acid. This change reduces the milk's pH value. When the pH falls far enough, casein (milk protein) falls out of solution as white curds. This can be done quickly to produce cottage cheese by adding an edible weak acid, like vinegar's acetic acid, directly to milk and waiting a few minutes. Figure 10-16 shows the result of the curds that form after they are filtered away from the whey and liquid.

In the next unit, we will examine another large category of reactions, the oxidation and reduction reactions that characterize much of the chemistry of the metals.

Unit 10: Acids and Bases—The Voyage of the Proton

Section 12: Further Reading

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