# Acid Strength And Molecular Structure

## Acid Strength and Percent Ionization

Do not confuse the term acid strength with pH. The strength of an acid has to do with the percentage of the initial number of acid molecules that are ionized. If a higher percentage of the original acid molecules are ionized, and therefore, donated as hydrated protons (hydronium ions) then the acid will be stonger. Strong acids are Hydrochloric (HCl(aq)), Hydrobromic (HBr(aq)), Nitric ($HNO_3$), Sulfuric ($H_2SO_4$), and Perchloric ($HClO_4$) acids. In each of these molecular acids the percentage of ionization is almost 100%.

On the other hand, there are certain acids that will not ionize very easily when added to water. These acids will only give up there protons to water with difficulty. For example, acetic acid (HC2H3O2), Hydrofluoric acid (HF(aq)), HydroCyanic (HCN), Carbonic acid ($H_2CO_3$), Sulfurous acid ($H_2SO_3$), and Nitrous acid ($HNO_2$) are only a few of the many "weak" acids. They will only allow 1-5% ionization. In other words, if 5% ionizatiuon takes place only 5 molecules out of 100 will ionize. The other 95 molecules go into solution as "molecules" and not ions. Weak acids can exhibit low pH readings just as strong acids. Acid strength of weak acids has more to do with the value of the ionization constant of the acid.

## Acid Strength and Equilibrium Constant

For the following weak acid according to the Law of Chemical Equilibrium:

$$HA + H_2O = H_3O^+ + A^-$$

ionization constant = $K_a = [H_3O^+]\ [A^-] / [HA]$

The larger the value of $K_a$ the more Hydronium ion will be in the solution for a given initial concentration of the acid since the value of $K_a$ must equal the ionization expression on the right side of the above equation and the Hydronium ion concentration is in the top portion of that expression. The percentage of ioninzation will therefore be larger. Strong acids have $K_a$'s that approach infinity in value. Therefore the percentage of ionization would approach 100% for strong acids.

## Relative Strengths of Acids and Bases

To understand why the $K_a$ approaches infinity in value, let's compare the acid strengths of the components in the solution capable of acting as an acid. For example in HCl:

$HCl + H_2O$ -----> $H_3O^+ + Cl^-$

HCl is giving up a Hydrogen ion to water to produce Chloride ion as the reaction proceeds to the right. Water is acting as the base accepting the Hydrogen ion to form Hydronium ion (Hydrated proton). Let's assume that we could reverse this process and proceed to the left. If so then the acid in the reverse process would be $H_3O^+$ as it would have to donate a Hydrogen ion to produce H2O. Now if we compare the acid strength between HCl and $H_3O^+$ we find that there is no comparison in acid strength between HCl and $H_3O^+$. The HCl is so much more acidic that $H_3O^+$ has no chance, and for all practical purposes, the reaction only proceeds to the right. This is true of any aqueous solution of a strong acid. Since the process only proceeds to the right then the concentration of the ions on the right side would be high compared to the concentration of the HCl which would approach zero. We know that if we placed that zero in the denominator of the equilibrium expression that would make the expression approach infinity since mathematically division by zero equals infinity.

We can come to the same conclusion if we look at the bases in the process. We identified the $H_2O$ in the above reaction as the base as the reaction proceeded to the right. If the reaction was able to reverse and proceed to the left then $Cl^-$ would have to accept a Hydrogen ion to become HCl. We say that the Chloride ion is the conjugate base of the acid HCl. If we compared the base strength of $H_2O$ to Chloride, water would be a much stronger base and that is another reason that this reaction would proceed exclusively to the right. So we can compare relative strengths between the bases and come to the same conclusion. We can say that HCl is the acid of the conjugate base Chloride ion. We say that the $H_3O^+$ is the conjugate acid of the base water. We have two conjugate pairs in any acid-base reaction.

Notice that the weaker the base the stronger is its conjugate. A conjugate pair in the above ionization of HCl is $HCl/Cl^-$. HCl is the stronger acid (compared to $H_3O^+$) and Chloride is the weaker base (compared to water). The other conjugate pair is between $H_2O/H_3O^+$. We found that $H_3O^+$ was the weaker acid (compared to HCl) but that $H_2O$ was the stronger base (compared to $Cl^-$)

In general, in any conjugate pair, a strong acid will be paired with a weak base, and a weak acid will be paired with a strong base. Also in any acid base reaction, the strong acid and strong base always proceeds to the weaker acid and base since the strong acid and base are better able to function as acid and base. The greater the difference in the relative strength of the two acids the more one sided will be the process. Strong acids and bases always proceed exclusively in one direction (toward the weaker acid and base). These last two paragraphs above are most profound and will be used in Organic systems as well.

Weaker acids ionizing in water will not be as acidic and therefore the conjugate acid, $H_3O^+$, will be able to compete and the reverse process will have a chance to occur. An equilibrium will form with any weak acid or weak base.

We can compare the relative strengths of acids or bases by comparing their ionization constants ($K_a$'s or $K_b$'s). The larger the ionization constant the stronger will be the acid or base. However, the question arises as to what causes one acid to be stronger than another or one base to be stronger than another base?

# Relative Acid Strength and Bond Strengths

For acids, this has to do with the strength of the bond holding the Hydrogen to the molecule. When that bond breaks it always breaks heterolytically. That means that both bonding electrons go to the more electronegative atom which is usually an Oxygen, Halogen, Sulfur, or carbon. When the bond breaks the Hydrogen atom is left without any electrons, a naked proton. Naked protons are not very stable so must be stablized or protected by surrounding itself with solvent molecules forming a "solvent cage". For aqueous acids that would be water. The negative end of the polar water molecules are attracted to the positive charge of the proton.

For stronger acids the bond is weaker and breaks more easily. The weaker the acid the stronger is the bond between its Hydrogens and the rest of the molecule. We can trace the strength of this bond to the molecular structure of the acid or base.

# Acid Strength and Atom Size

When the bond breaks between a Hydrogen atom and another atom, both bonding electrons will go to the other atom giving it a negative charge. The larger this atom the greater will be its surface area. The negative charge can be dispersed over this larger surface area and thereby be stabilized. The more stabilized this anion the less likely it will react with the Hydrogen ion to reverse the process. In general if we compare acids with the other atoms are in the same group of the periodic table, the further down in the group the atom is the stronger will be the acid. For example the relative acid strength of the Hydrogen halides is

HI > HBr > HCl > HF.

In group 16 (VIA)

$H_2Te > H_2Se > H_2S > H_2O$

For Group 15(VA)

$SbH_3 > AsH_3 > PH_3 > NH_3$

# Relative Acid Strength and Electronegativity

If we compared acid strength with acids where the atoms bonded to Hydrogen were in the same period, the difference in the size of the atoms would not be significant. In that case the electronegativity becomes the deciding factor. The greater the electronegativity of the atom the stronger will be the acid. The larger difference in electronegativity between the Hydrogen and the other atom shifts the bonding pair of electrons toward the other atom thus weakens the bond between the Hydrogen and the other atom. Therefore, the bond between the atom and Hydrogen will be more easily broken.

For example:

$HF > H_2O > NH_3 > CH_4$

$HCl > H_2S > PH_3 > SiH_4$

# Relative Acid Strengths of Oxyacids and Electronegativity

Oxyacids have the Hydrogen atoms in the acid bonded to an Oxygen. The more Oxygens there are in the acid the stronger the acid will be. This can be understood by noting that Oxygen atoms are extremely electronegative. The greater number of Oxygens in the molecule the greater the shift of electrons toward the Oxygens and the weaker the bond between the Hydrogens bonded to Oxygens becomes.

The relative acid strength of the following Oxyacids verifys this trend:

$H_2SO_4$ is a stronger acid than $H_2SO_3$

$HNO_3$ is a stronger acid than $HNO_2$

$HClO_4$ is a stronger acid than $HClO_3$ is a stronger acid than $HClO_2$ is a stronger acid than HClO