

The Fall of the Proton

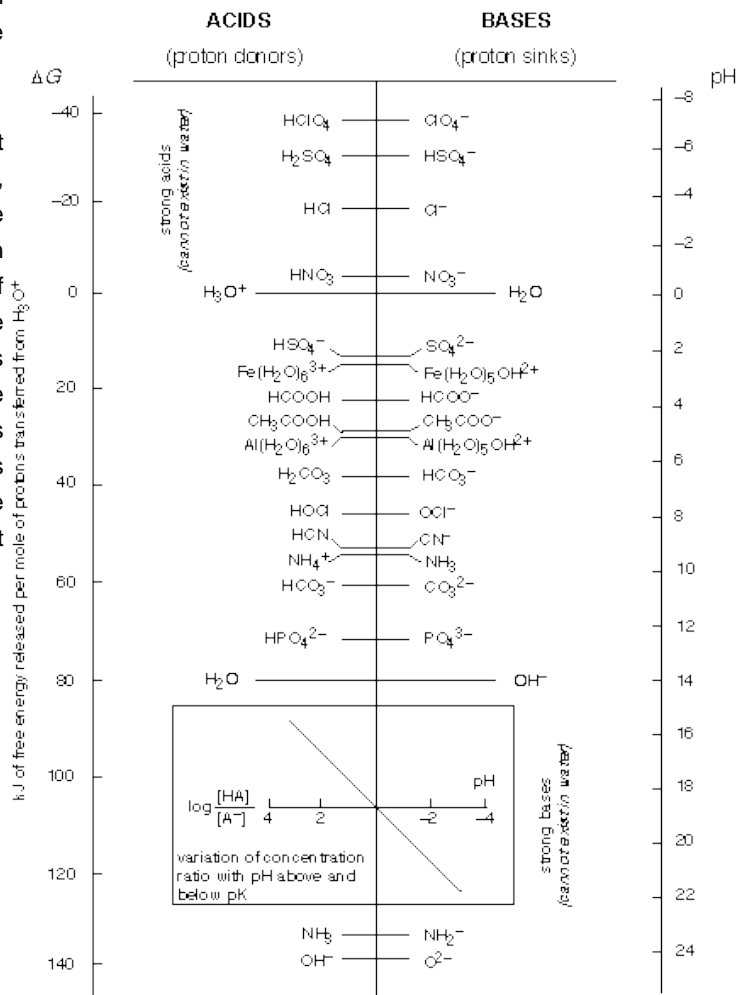
An **acid**, being a proton donor, can only *act* as an acid if there is a suitable **base** present to accept the proton. What do we mean by "suitable" in this context? Simply that a base, in order to accept a proton, must provide a lower-energy resting place for the proton. (We are actually referring to something called "free energy" here, but don't worry about that if you are not familiar with that term; just think of it as a form of potential energy.) **Thus you can view an acid-base reaction as the "fall" of the proton from a higher potential energy to a lower potential energy--** the same as a book will fall (if you drop it) only downward, to a position of lower (gravitational) potential energy.

Sources and Sinks

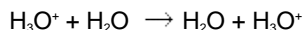
Viewed in this way, **an acid is a proton source, a base is a proton sink.** The tendency for a proton to move from source to sink depends on how far the proton can fall in energy, and this in turn depends on the energy difference between the source and the sink. This is entirely analogous to measuring the tendency of water to flow down from a high elevation to a lower one; this tendency (which is related to the amount of energy that can be extracted in the form of electrical work if the water flows through a power station at the bottom of the dam) will be directly proportional to the difference in elevation (difference in potential energy) between the source (top of the dam) and the sink (bottom of the dam).

Now look at the diagram at the right and study it carefully. In the center columns of the diagram, you see a list of acids and their conjugate bases. These acid-base pairs are plotted on an energy scale which is shown at the left side of the diagram. This scale measures the free energy released when one mole of protons is transferred from a given acid to H_2O . Thus if one mole of HCl is added to water, it dissociates completely and heat is released as the protons fall from the source (HCl) to the lower free energy that they possess in the H_3O^+ ions that are formed when the protons combine with H_2O .

Any acid shown on the left side of the vertical line running down the center of the diagram can donate protons to any base (on the right side of the line) that appears below it. The greater the vertical separation, the greater will be the fall in free energy of the proton, and the more complete will be the proton transfer at equilibrium.



Notice the $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ pair shown at zero kJ on the free energy scale. This zero value of free energy corresponds to the proton transfer process



which is really no reaction at all, hence the zero fall in free energy of the proton. Since the proton is equally likely to attach itself to either of two identical H_2O molecules, the equilibrium constant is unity.

Now look at the acid/base pairs shown at the top of the table, above the $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ line. All of these acids can act as proton sources to those sinks (bases) that appear below them. Since H_2O is a suitable sink for these acids, all such acids will lose protons to H_2O in aqueous solutions. These are therefore all strong acids that are 100% dissociated in aqueous solution; this total dissociation reflects the very large equilibrium constants that are associated with any reaction that undergoes a fall in free energy of more than a few kilojoules per mole.

Leveling effect

Because H_2O serves as a proton sink to any acid in which the proton free energy level is greater than zero, the strong acids such as HCl and H_2SO_4 cannot "exist" (as acids) in aqueous solution; they exist as their conjugate bases instead, and the only proton donor present will be H_3O^+ . This is the basis of the **leveling effect**, which states that **the strongest acid that can exist in aqueous solution is H_3O^+** .

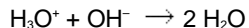
Dissociation of weak acids

Now consider a **weak acid**, such as HCN at about 50 kJ on the scale. This positive free energy means that in order for a mole of HCN to dissociate (transfer its proton to H_2O), the proton must gain 40 kJ of free energy per mole. In the absence of a source of energy, the reaction will simply "not go"; HCN dissociates only to a minute extent in water.

Why is a weak acid such as HCN dissociated at all? The molecules in solution are continually being struck and bounced around by the thermal motions of neighboring molecules. Every once in a while, a series of fortuitous collisions will provide enough kinetic energy to a HCN molecule to knock off the proton, effectively boosting it to the level required to attach itself to water. This process is called **thermal excitation**, and its probability falls off very rapidly as the distance (in kJ) that the proton must rise increases. The protons on a "stronger" weak acid such as HSO_4^- or CH_3COOH will be thermally excited to the H_3O^+ level much more frequently than will the protons on HCN or HCO_3^- , hence the difference in the dissociation constants of these acids.

Titration

Although a weak acid such as HCN will not react with water to a significant extent, you are well aware that such an acid can still be titrated with strong base to yield a solution of NaCN at the equivalence point. To understand this process, find the $\text{H}_2\text{O}-\text{OH}^-$ pair at about 80 kJ on the free energy scale. Because the OH^- ion can act as a proton sink to just about every acid shown on the diagram, the addition of strong base in the form of NaOH solution allows the protons at any acid above this level to fall to the OH^- level according to the reaction

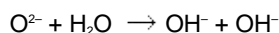


Titration, in other words, consists simply in introducing a low free energy sink that can drain off the protons from the acids initially present, converting them all into their conjugate base forms.

Strong bases

There are two other aspects of the H_2O - H_3O^+ pair that have great chemical significance. First, its location at 80 kJ/mol tells us that for a H_2O molecule to transfer its proton to another H_2O molecule (which then becomes a H_3O^+ ion whose relative free energy is zero), a whopping 80 kJ/mol of free energy must be supplied by thermal excitation. This is so improbable that only one out of about 10 million H_2O molecules will have its proton elevated to the H_3O^+ level at a given time; this corresponds to the small value of the ion product of water, about 10^{-14} .

The other aspect of the H_2O - OH^- pair is that its location means the **hydroxide ion is the strongest base that can exist in water**. On our diagram only two stronger bases (lower proton free energy sinks) are shown: the amide ion NH_2^- , and the oxide ion O^{2-} . What happens if you add a soluble oxide such as Na_2O to water? Since O^{2-} is a proton sink to water, it will react with the solvent, leaving OH^- as the strongest base present:



This again is the leveling effect; all bases stronger than OH^- appear equally strong in water, simply because they are all converted to OH^- .

Proton free energy and pH

The pH of a solution is more than a means of expressing its hydrogen ion concentration on a convenient logarithmic scale. The concept of pH was suggested by the Swedish chemist Sørensen in 1909 as a means of compressing the wide range of $[\text{H}^+]$ values encountered in aqueous solutions into a convenient range. The modern definition of pH replaces $[\text{H}^+]$ with $\{\text{H}^+\}$ in which the curly brackets signify the effective concentration of the hydrogen ion, which chemists refer to as the hydrogen ion activity

$$\text{pH} = \log \{\text{H}^+\}$$

The real physical meaning of pH is that it measures the **availability** of protons in the solution; that is, the ability of the solution to supply protons to a base such as H_2O . This is the same as the "hydrogen ion concentration" $[\text{H}^+]$ only in rather dilute solutions; at ionic concentrations greater than about 0.001M, electrostatic interactions between the ions cause the relation between the pH (as measured by direct independent means) and $[\text{H}_3\text{O}^+]$ to break down. Thus we would not expect the pH of a 0.100 M solution of HCl to be exactly 1.00.

On the right side of the illustration is a pH scale. At the pH value corresponding to a given acid-base pair, the acid and base forms will be present at equal concentrations. For example, if you dissolve some solid sodium sulfate in pure water and then adjust the pH to 2.0, about half of the SO_4^{2-} will be converted into HSO_4^- . Similarly, a solution of Na_2CO_3 in water will not contain a very large fraction of CO_3^{2-} unless the pH is kept above 10.

Suppose we have a mixture of many different weak acid-base systems, such as exists in most biological fluids or natural waters, including the ocean. The available protons will fall to the lowest free energy levels possible, first filling

the lowest-energy sink, then the next, and so on until there are no more proton-vacant bases below the highest proton-filled (acid) level. Some of the highest protonated species will donate protons to H_2O through thermal excitation, giving rise to a concentration of H_3O^+ that will depend on the concentrations of the various species. The equilibrium pH of the solution is a measure of this concentration, but this in turn reflects the relative free energy of protons required to keep the highest protonated species in its acid form; it is in this sense that pH is a direct measure of proton free energy.

In order to predict the actual pH of any given solution, we must of course know something about the nominal concentrations C_a of the various acid-base species, since this will strongly affect the distribution of protons. Thus if one proton-vacant level is present at twice the concentration of another, it will cause twice as many acid species from a higher level to become deprotonated. In spite of this limitation, the proton free energy diagram provides a clear picture of the relationships between the various acid and base species in a complex solution.

Source: http://chemwiki.ucdavis.edu/Physical_Chemistry/Acids_and_Bases/Acid%2F%2FBase_Reactions/The_Fall_of_the_proton