

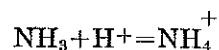
THE BASICITY OF WATER

L. S. Guss
South Dakota State College

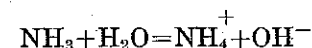
The concept of acids and bases has gone through a number of interesting changes since the beginnings of modern chemistry and even at the present time, it is far from satisfactory. Prior to the time of Lavoisier, acids were considered as compounds having a number of properties in common, among which was the neutralization of substances known as bases. Lavoisier attempted to correlate acid properties with structure by demonstrating that oxygen was apparently an element common to all acids. This was shown to be false by the investigations of Davy on hydrochloric acid.

No satisfactory explanation of acid-base behavior was advanced after this time until Arrhenius developed the theory of ionization. Our present conventional concept, that acids and bases produce hydrogen and hydroxyl ions in water solution, is based on this theory. As long as one limits his interests to water solutions, this definition is quite satisfactory. However, organic chemists soon demonstrated that many nitrogen compounds are basic even in anhydrous solutions, so hydroxyl ions cannot be peculiar to bases. Later it was found that acid catalysis is dependent not only on hydrogen ions, but on undissociated molecules as well. Bronsted and Lowry extended the definition of acids and bases to cover these cases. According to their proton concept, acids are substances capable of giving up protons to substances known as bases. Bases, then, are any substances which can unite with protons.

According to Bronsted, ammonia is a base, not because it is capable of ionizing as ammonium hydroxide, but because it can unite with protons to form ammonium ions:



On dissolving ammonia in water, we can detect the presence of hydroxyl ions because the ammonia has removed protons from water:

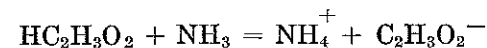


It has been demonstrated that free hydrogen ions cannot exist alone in solution, but that they unite with the solvent unless other stronger bases are present. Thus, the dissociation of a strong acid in water is in reality a double decomposition, resulting in a transfer of a proton to the water molecule:



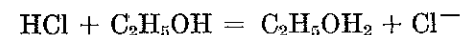
This hydrated hydrogen ion, known as the oxonium ion, is the source of acid properties in water solution. The strength of an acid is thus dependent on the basicity of the water as well as the tendency of the acid to give up protons.

Water is a weaker base than liquid ammonia. Thus, while acetic acid is only slightly dissociated in water, it is a strong acid in ammonia:



On the other hand, alcohol is a weaker base than water, for nitric acid, which is a strong acid in water, is only partially dissociated in alcohol. One would expect, therefore, that the addition of water to ethanol would have an effect analogous to the addition of ammonia to water.

If a strong acid, as HCl, is added to anhydrous alcohol, there is a transference of protons to the solvent:



On the addition of water to this solution, there is a tendency for the protons to be transferred to the water molecules, since the latter are more basic:



We can set down the expression of an equilibrium constant based on this equation:

$$\frac{[\text{C}_2\text{H}_5\text{OH}_2^+][\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]} = K$$

We recognize this as the hydrolysis constant of the "salt", H_3OCl . (Compare NH_4Cl .)

If an indicator, such as methyl orange, is put in the original ethanol solution, it acquires the red acid color. If we add a drop of water to this solution, we find an immediate color change to the alkaline yellow. This is entirely analogous to the addition of ammonia to a water solution. Hence, we find that our conventional idea of a base must be modified, for water, which we consider neutral, acts as a fairly strong base in a solvent such as alcohol.

If we let c represent the initial concentration of hydrochloric acid, then:

$$[C_2H_5OH_2^+] = c - [H_3O^+] = \frac{cK}{K + [H_2O]}$$

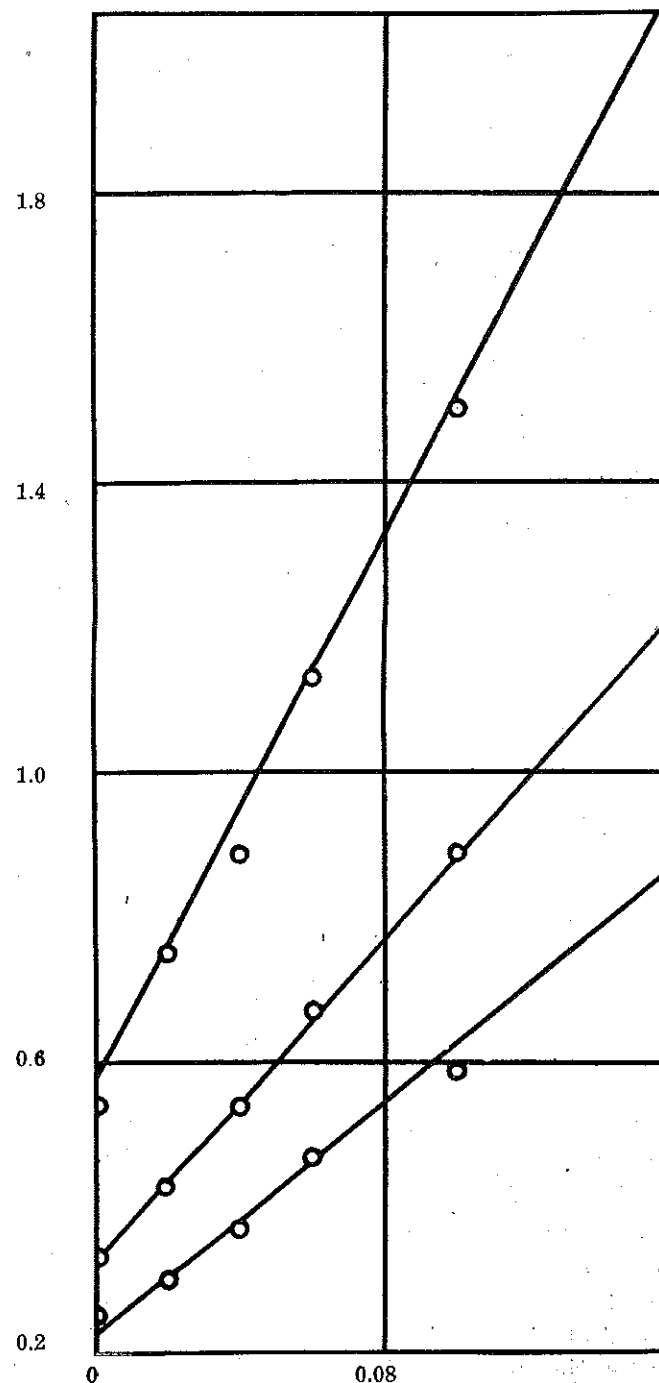
If we let HI and I represent the formulas of the acid and basic forms of an indicator:

$$\frac{[I]}{[HI]} = \frac{K_I}{[C_2H_5OH_2^+]} = K_I \left\{ \frac{K + [H_2O]}{cK} \right\} = \frac{K_I}{Kc} [H_2O] - \frac{K_I}{c}$$

If we plot values of $\frac{[I]}{[HI]}$ against $[H_2O]$, we should get a

straight line. The accompanying graph, which shows such data for the indicator methyl yellow, indicates that this is true for three different acid concentrations. We notice that

the intercept is $\frac{K_I}{c}$ and this divided by the slope gives a value of $K=0.06$.



Effect of Water on Methyl Yellow in Ethanol