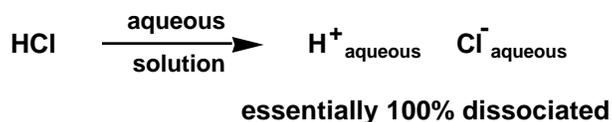
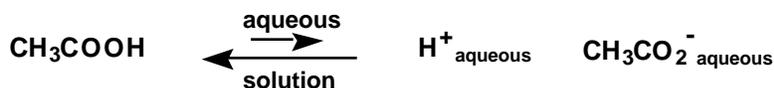


Text Related to Segment 11.01 ©2002 Claude E. Wintner

The concepts of acidity and basicity are universal in chemistry and reach back to the very beginnings of the study of the discipline. Indeed, in some sense our entire understanding of chemical reactivity may be said to be rooted in a broad interpretation of these two antipodal ideas. To begin with the most familiar situation of aqueous solution, according to the oldest and still perhaps the simplest (if considerably limited) definition an acid is any molecule which, when dissolved in water, yields some concentration of protons (hydrogen cations) greater than the hydroxide anion concentration; a base is any molecule which, when dissolved in water, yields some concentration of hydroxide ions greater than the proton concentration. Thus, hydrogen chloride, HCl, when dissolved in water, dissociates essentially completely into protons and chloride ions and therefore is said to be a very strong acid:



On the other hand, the molecule acetic acid, CH₃COOH, ionizes to a considerably lesser extent; it is a weaker acid than HCl. (We shall discuss below why acetic acid is even as acidic as it is.) Of one thousand (10³) molecules of one molar aqueous acetic acid at room temperature, on average just four molecules are ionized at any one time. This fact is most easily expressed quantitatively by means of an equilibrium constant: $K_A = 1.8 \times 10^{-5}$, and also — in order to be in the realm of small positive integers — as the negative of the logarithm of the equilibrium constant, termed pK_A. Thus, for acetic acid at room temperature pK_A is 4.8:



For 1 molar aqueous acetic acid at room temperature:

$$K_A = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]} = \frac{4.2 \times 10^{-3} \times 4.2 \times 10^{-3}}{(\approx) 1} = 1.8 \times 10^{-5}$$

$$\text{p}K_A = -\log K_A = -(0.25 - 5) = 4.8$$

Water itself ionizes only very slightly, far less than does even acetic acid, to yield both protons and hydroxide ions. To consider it for the moment as an acid, water is a much weaker acid than is acetic acid: of 100 million (10^8) molecules of water at room temperature, on average only one is ionized at any given time. The equilibrium constant K_A is 1.8×10^{-16} , and thus for pure water at room temperature $\text{p}K_A$ is 15.8. Note that the weaker the acid, the larger the value of the $\text{p}K_A$.

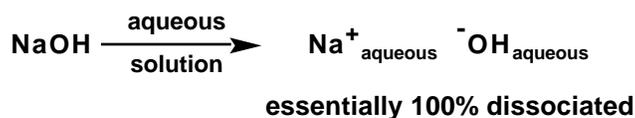


At room temperature:

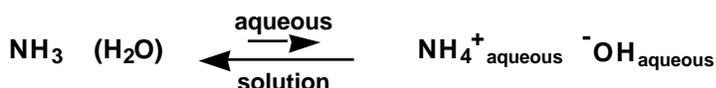
$$K_A = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.5} = 1.8 \times 10^{-16}$$

$$\text{p}K_A = -\log K_A = -(0.25 - 16) = 15.8$$

To speak now of bases, when sodium hydroxide, NaOH, is dissolved in water, it dissociates essentially completely into sodium cations and hydroxide ions:



However, when the weaker base ammonia is dissolved in water at room temperature at a one molar concentration, for each one thousand molecules of ammonia, approximately only four hydroxide ions are formed. Again an equilibrium constant is useful. In this case K_B is 1.8×10^{-5} , and pK_B is 4.8. (That this value of 4.8 is the same as the corresponding one for acetic acid is nice for the sake of remembrance, but it is a simple coincidence!)

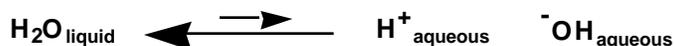


For 1 molar aqueous ammonia at room temperature:

$$K_B = \frac{[\text{NH}_4^+][^-\text{OH}]}{[\text{NH}_3]} = \frac{4.2 \times 10^{-3} \times 4.2 \times 10^{-3}}{(\approx 1)} = 1.8 \times 10^{-5}$$

$$pK_B = -\log K_B = -(0.25 - 5) = 4.8$$

Water is as weak a base as it is an acid: at room temperature K_B is 1.8×10^{-16} , and pK_B is 15.8:



At room temperature:

$$K_B = \frac{[\text{H}^+][^-\text{OH}]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.5} = 1.8 \times 10^{-16}$$

$$pK_B = -\log K_B = -(0.25 - 16) = 15.8$$

Finally, the familiar expression of the "ion product" constant for water:

$$K_W = [\text{H}^+][^-\text{OH}] = 10^{-7} \times 10^{-7} = 10^{-14}$$

is a restatement of the water equilibrium expression for aqueous solutions, but leaving out the essentially constant molarity of water in all such situations. On the basis of either expression there is a most important point to be kept in mind, and especially when mechanisms for chemical reactions involving these ubiquitous species are being proposed. Thus, one never can expect protons (that is, hydrogen cations or, equivalently, hydronium ions) to exist in any significant concentration in the presence of an excess of hydroxide ions. For example, if the proton concentration is just 10^{-3} , then — to obey the expression — the hydroxide ion concentration must be the vanishingly small 10^{-11} . Conversely, if the hydroxide ion concentration is 10^{-3} , then the proton concentration must be 10^{-11} . In effect, then, this is the quantitative basis for the old definition, as stated already at the outset, that in an acid there is a concentration of protons greater than the hydroxide anion concentration and in a base there is a concentration of hydroxide ions greater than the proton concentration. *In the course of a mechanistic explanation of a reaction, do not invoke the proton as a viable species in basic solution! And, do not invoke hydroxide ion as a viable species in acid!*

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