14.1: Prelude to Ionization of Water

We have already noted the importance of reactions in aqueous solutions in the chemical laboratory, in the natural environment, and in the human body. Many reactions in aqueous solutions involve weak acids or bases or slightly soluble substances, and in such cases one or more equilibria are achieved in solution.

Furthermore, the equilibrium state is usually reached almost instantaneously, and so we can use the equilibrium law to calculate the concentrations and amounts of substance of different species in solution. Such information enables us to understand, predict, and control what will happen in solution, and it has numerous practical applications. Equilibrium constants may be used to obtain information about reactions in solution, and in many cases the results of equilibrium calculations will be applied to practical problems.

Acid-base reactions in aqueous solutions are intimately related to water's ability to act as both a weak acid and a weak base, producing H_3O^+ and OH^- by proton transfer. In any aqueous solution at 25°C, the equilibrium constant of water (k_w) is as follows:

$$K_w = [\, H_3O^+][OH^-] = \frac{1.00 \times 10^{-14}}{1 \text{ mol L}^{-1}}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

and concentrations of H_3O^+ and OH^- can vary from roughly 10^0 to 10^{-14} mol/L. This makes it convenient to define pH and pOH as:

$$pH = -\log \frac{[\, H_3O^+]}{1 \text{ mol L}^1} \tag{14.1.1}$$

$$\tag{14.1.2}$$

$$pOH = -\log \frac{[\, OH^-]}{1 \text{ mol L}^{-1}} \tag{14.1.3}$$

Since molecules of a strong acid transfer their protons to water molecules completely, $[H_3O^+]$ (and hence pH) can be obtained directly from the stoichiometric concentration of the solution. Similarly $[OH^-]$ and pOH may be obtained from the stoichiometric concentration of a strong base. In the case of weak acids and weak bases, proton-transfer reactions proceed to only a limited extent and a dynamic equilibrium is set up. In such cases an acid constant K_a (equilibrium constant for acids) or a base constant K_b as well as the stoichiometric concentration of weak acid or base are required to calculate $[H_3O^+]$, $[OH^-]$, pH, or pOH. K_a and K_b for a conjugate acid-base pair are related, and their product is always K_w.

Often it is necessary or desirable to restrict the pH of an aqueous solution to a narrow range. This can be accomplished by means of a buffer solution—one which contains a conjugate weak acid-weak base pair. If a small amount of strong base is added to a buffer, the OH^- ions are consumed by the conjugate weak acid, so they have little influence on pH. Similarly, a small amount of strong acid can be consumed by the conjugate weak base in a buffer. To a good approximation the $[H_3O^+]$ in a buffer solution depends only on K_a for the weak acid and the stoichiometric concentrations of the weak acid and weak base.

Indicators for acid-base on are conjugate acid-base pairs, each member of which is a different color. An indicator changes from the color of the conjugate acid to the color of the conjugate base as pH increases from approximately $pK_{In} - 1$ to $pK_{In} + 1$. For titrations involving only strong acids and strong bases, several indicators are usually capable of signaling the endpoint because there is a large jump in within ± 0.05 L of the exact stoichiometric volume of titrant. In the case of titrations which involve a weak acid or a weak base, a buffer solution is involved and the jump in pH is smaller. Consequently greater care is required in selection of an appropriate indicator.

A dynamic equilibrium is set up when a solid compound is in contact with a saturated solution. In the case of an ionic solid, the equilibrium constant for such a process is called the solubility product. K_{sp} can be determined by measurement of the solubility of a compound, and it is useful in predicting whether the compound will precipitate when ionic solutions are mixed. The common-ion effect, in which an increase in the concentration of one ion decreases the concentration of the other ion of an insoluble compound, can be interpreted quantitatively using solubility products. It is also true that removal of one ion of an insoluble compound from solution will increase the concentration of the other ion, and hence the solubility. It is for this reason that salts of weak acids often dissolve in acidic solutions—protonation of the anion effectively reduces its concentration to the point where the solubility product is not exceeded.

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