8.1: What Factors Control Reactions

The key to understanding the behavior of chemical reactions is to remember that:

a. chemical reactions are systems in which reactants and products interact with their environment and
b. at the molecular level, all reactions are reversible, even though some reactions may seem irreversible.

For example, once a log starts burning, we cannot easily reassemble it from carbon dioxide ($\mathrm{CO_2}$), water ($\mathrm{H_2O}$), and energy. But in fact, we can reassemble the log in a fashion by allowing a tree to grow, and by using $\mathrm{CO_2}$ from the air, $\mathrm{H_2O}$ from the ground, and energy from the sun (photosynthesis). However, this type of reverse (or backward) reaction is far more complex and involved than the simple forward reaction of burning.

There are, however, a number of factors that we can use to predict how fast and how far a particular reaction will go, including the concentration of the reactants, the temperature, the type of reaction, and the presence of a catalyst. The concentrations of molecules and the temperature of the system are important because all reactions involve collisions between molecules (except for reactions driven by the absorption of light—and you could view those as collisions of a sort). The concentration of reactants determines how often various types of collisions take place (i.e., the more molecules per unit volume, the more frequently collisions occur), whereas the temperature determines the energetics of the collisions: recall that there is a distribution of kinetic energies of molecules at a particular temperature, so not all collisions will lead to a reaction. Molecular structure also matters because it determines whether or not collisions are productive. The only collisions that work are those in which molecules hit each other in particular orientations and with particular energies.

As a reaction proceeds, and reactants are converted into products, the probability of reactant molecules colliding decreases (since there are fewer of them) while the probability of product molecules colliding increases. That is the rate of the forward reaction slows down and the rate of the reverse reaction speeds up This will continue until the rates of the forward reaction and the backward reaction are equal, and the system reaches equilibrium: the point at which no more macroscopic changes occur and the concentrations of reactants and products remain constant at the macroscopic scale.[1] However, as we will discuss further, the forward and back reactions have not stopped, and if we could see the molecules we would see both forward and back reactions still occurring, although there is no overall change in concentration.

As an example, Brønsted–Lowry acid–base reactions are very fast because the probability that the reaction occurs per unit of time is high. When an acid and a base are mixed together, they react immediately with no waiting and without the addition of heat. For example, if we dissolve enough hydrogen chloride gas (HCl) in water to make a $0.1\ \mathrm{M}$ solution of hydrochloric acid, the pH immediately drops from 7 (the \mathrm{pH}\) of water) to 1.[2] This measurement tells us that all the HCl has ionized, to give: $\left[\mathrm{H}^{+}\right]=0.1$ and $\left[\mathrm{Cl}^{-}\right]=0.1$.

Now let us take the case of acetic acid ($\mathrm{CH_3COOH}$). If we dissolve enough acetic acid in water to make a $0.1-\mathrm{M}$ solution, the pH of the solution immediately changes from $\mathrm{pH} 7$ (pure water) to 2.9 (not 1). Even if you wait (as long as you want) the pH stays constant, around 3. You might well ask, "What is going on here?" The acid–base reaction of acetic acid and water is fast, but the pH is not as low as you might have predicted. We can calculate the $\left[\mathrm{H}^{+}\right]$ from the pH, again using the relationship $\mathrm{pH}=-\log\left[\mathrm{H}^{+}\right]$ and \left[\mathrm{H}^{+}\right] = 10^{-\mathrm{pH}}\), giving us a value of $\left[\mathrm{H}^{+}\right]=1.3\times10^{-3}\ \mathrm{M}$. Thus, the concentration of H^{+} is more than two orders of magnitude less than you might have expected! If you think about this, you will probably conclude that the amount of acetic acid (AcOH)[3] that actually reacted with the water must have been very small indeed. In fact we can calculate how much acetic acid reacted using the relationships from the equation:

$$\mathrm{AcOH}+\mathrm{H_2O}\rightleftarrows\mathrm{H_3O^{+}}+\mathrm{AcO^{-}} \tag{8.1.1}$$

If the concentration of acetic acid started at $0.10\ \mathrm{M}$, and after the ionization reaction $1.3\times10^{-3}\ \mathrm{M}$ of H^{+} are present, then the final concentration of acetic acid must be $(0.10 \text{ minus } 1.3$\tiems$10^{-3})\ \mathrm{M}$. If we use the appropriate number of significant figures, this means that the concentration of acetic acid is still $0.10\ \mathrm{M}$ (actually $0.0986\ \mathrm{M}$).

There are two important conclusions here: first, the reaction of acetic acid is fast, and second, most of the acetic acid has not, in fact, reacted with the water. But wait—there is more! Even if the reaction appears to have stopped because the pH is not changing any further, at the molecular level things are still happening. That is, the reaction of acetic acid with water continues on, but the reverse reaction occurs at the same rate. So the bulk concentrations of all the species remain constant, even though individual molecules present in each population are constantly changing.[4] The questions of how far a reaction proceeds (towards products) and how fast it gets there are intertwined. We will demonstrate the many factors that affect these two reaction properties.

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Questions to Answer

- Draw out a general Brønsted–Lowry acid–base reaction that might occur in water.
- Why do you think the reaction occurs so fast (as soon as the molecules bump into each other)?
- Do you think the water plays a role in the reaction? Draw out a molecular-level picture of your acid–base reaction, showing the solvent interactions.

Question to Ponder

- How do you think the reaction would be affected if it took place in the gas phase instead of an aqueous solution?
