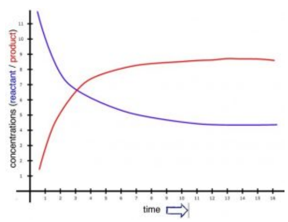
8.2: Reaction Rates

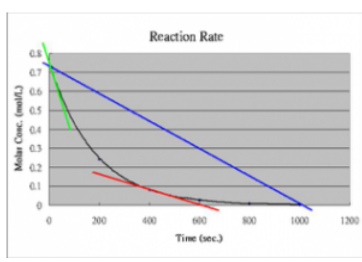
In science, when we talk about a rate we mean the change in a quantity over time. A few non-chemical examples include: certain investments with an interest rate, which is the increase in the principle over time (if the rate is negative, then it means that the amount of principle is decreasing over time—not a good investment!); your speed, which is the rate at which you travel down the road, given in miles per hour (or kilometers per hour); a child's growth rate, which might be an inch or two per year (while the elderly might shrink at a different rate); and the growth rate of some plants, like kudzu, which can grow at a rate of 12 inches per day. The units of rate are an amount divided by a period of time. This might seem too obvious to dwell on, but it is worth noting that most real processes do not have a constant rate of change; rates themselves can and do change. This is one reason why calculus is useful in chemistry: it provides the mathematical tools needed to deal with changing rates, like those associated with planetary motions, falling bodies, and (it turns out) chemical reactions.

If we apply the idea of an amount divided by a period of time to the speed of a chemical reaction, what can we measure to determine a reaction's rate? What units tell us the amount present, in the same way that miles and meters measure distance? We can't use mass, because reactions occur between particles (atoms, molecules, ions), which have different masses. We must use the unit that tells us how many particles of a particular type there are—moles. Furthermore, because most reactions (particularly the ones involved in biological and environmental systems) occur in aqueous solutions or in the atmosphere, we usually use units of concentration—molarity (M, $\mathrm{mol/L}$)—to describe the amount of a substance taking part in or produced by a reaction. Typically, the concentration of substance $\mathrm{A_2}$ is written $[\mathrm{A_2}]$, and the rate of a reaction can be described as the change in concentration of a reactant or product over a unit of time. So, $\Delta[\mathrm{A_2}]/\Delta\mathrm{t}$ or $[\mathrm{A_2}]_2 - [\mathrm{A2_2}]_1/t_2 - t_1$, , where $[\mathrm{A_2}]_2$ is the concentration at time t_2, and $[\mathrm{A_2}]_1$ is the concentration at time t_2 (assuming that t_2 occurs later in time than t_1).

Reaction Rates and Probabilities



Let us now step back and think about what must happen in order for a reaction to occur. First, the reactants must be mixed together. The best way to make a homogeneous mixture is to form solutions, and it is true that many reactions take place in solution. When reactions do involve a solid, like the rusting of iron, the reactants interact with one another at a surface. To increase the probability of such a reaction, it is common to use a solid that is very finely divided, so that it has a large surface area and thus more places for the reactants to collide.[5]



We will begin with a more in-depth look at reaction rates with a simple hypothetical reaction that occurs slowly, but with a reasonable rate in solution. Our hypothetical reaction will be $\mathrm{A_2 + B_2 \rightleftarrows 2AB}$. Because the reaction is slow, the loss of reactants ($\mathrm{A_2 + B_2}$) and the production of product (AB) will also be slow, but measurable. Over a reasonable period of time, the concentrations of $\mathrm{A_2}$, $\mathrm{B_2}$, and AB change significantly. If we were to watch the rate of the forward reaction ($\mathrm{A_2 + B_2 \rightleftarrows 2AB}$), we would find that it begins to slow down. One way to visualize this is to plot the concentration of a reactant versus time (as shown in the graph). We can see that the relationship between them is not linear, but falls off gradually as time increases. We can measure rates at any given time by taking the slope of the tangent to the line at that instant.[6] As you can see from the figure, these slopes decrease as time goes by; the tangent at time = 0 is much steeper than the tangent at a later time. On the other hand, immediately after mixing $\mathrm{A_2 + B_2}$, we find that the rate of the backward reaction (that is: $\mathrm{2AB \rightleftarrows\ A_2 + B_2}$) is zero, because there is no AB around to react, at least initially. As the forward reaction proceeds, however, the concentration of AB increases, and the backward reaction rate increases. As you can see from the figure, as the reaction proceeds, the concentrations of both the reactants and products reach a point where they do not change any further, and the slope of each concentration time curve is now 0 (it does not change and is "flat").

Let us now consider what is going on in molecular terms. For a reaction to occur, some of the bonds holding the reactant molecules together must break, and new bonds must form to create the products. We can also think of forward and backward reactions in terms of probabilities. The forward reaction rate is determined by the probability that a collision between an A_2 and a B_2 molecule will provide enough energy to break the $A—A$ and $B—B$ bonds, together with the probability of an AB molecule forming. The backward reaction rate is determined by the probability that collisions (with surrounding molecules) will provide sufficient energy to break the $A—B$ bond, together with the probability that $A—A$ and $B–B$ bonds form. Remember, collisions are critical; there are no reactions at a distance. The exact steps in the forward and backward reactions are not specified, but we can make a prediction: if these steps are unlikely to occur (low probability), the reactions will be slow.

As the reaction proceeds, the forward reaction rate decreases because the concentrations of A_2 and B_2 decrease, while the backward reaction rate increases as the concentration of AB increases. At some point, the two reaction rates will be equal and opposite. This is the point of equilibrium. This point could occur at a high concentration of AB or a low one, depending upon the reaction. At the macroscopic level, we recognize the equilibrium state by the fact that there are no further changes in the concentrations of reactants and products. It is important to understand that at the molecular level, the reactions have not stopped. For this reason, we call the chemical equilibrium state a dynamic equilibrium. We should also point out that the word equilibrium is misleading because in common usage it often refers to a state of rest. In chemical systems, nothing could be further from the truth. Even though there are no macroscopic changes observable, molecules are still reacting.[7]

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Questions to Answer

- What does linear mean (exactly) when referring to a graph?
- Imagine you are driving at a constant speed of 60 miles per hour. Draw a graph of distance versus time, over a time period of four hours.
- How would you determine your speed from the graph (assuming you did not already know the answer)?
- Now imagine you take your foot off the accelerator and the car coasts to a stop over the course of one hour. What is the average speed over the last hour? How would you figure that out?
- What is the speed exactly 30 minutes after you take your foot off the brake? How would you figure that out?
- Consider the reaction $A_2 + B_2 \rightleftarrows 2AB$. If the rate of the forward reaction $= -\Delta\left[A_2\right]/\Delta t$ (at a given time). How would you write the rate in terms of $[B_2]$ or in terms of $[AB]$?
- How does the rate of the forward reaction change over time? Does it increase, decrease or stay the same? Why?
- What does a probability of "0" mean?
- How do we know that, at equilibrium, the forward and reverse reactions are still occurring.
- Design an experiment that would allow you to investigate whether a reaction had stopped:at the macroscopic level and at the molecular level

Questions to Ponder

- Why can a macroscopic reaction be irreversible, even though at the molecular level reaction is reversible?
- Under what conditions (if any) would a reaction stop completely?
- Why are molecular level and macroscopic behaviors different?

Questions for Later

- Why do you think the amounts of products and reactants do not change after a certain time?
- What is the observable rate of reaction after the time when the concentrations of products and reactants change?

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