"Nothing endures but change."
Heraclitus

"Science is the tool of the Western mind and with it more doors can be opened than with bare hands."

C.G. Jung

Kinetics, Reaction Rates & Mechanisms

Any definition of chemistry will likely refer to the transformations of matter. An example would be something similar to "the study of substances and how they react when in contact with one another." You have witnessed countless chemical reactions throughout your life, and undoubtedly you have observed that some occur very quickly, such as when wood burns in a fireplace, and others occur very slowly, such as when the iron body of a car rusts. The study of the rates of chemical reactions and how they take place forms a subdiscipline within chemistry known as *chemical kinetics*.

Perhaps you have a bottle of hydrogen peroxide in your bathroom cabinet. It is usually stored in a brown bottle, and its label will have the instructions "store in a cool, dark place." These storage instructions are there because hydrogen peroxide undergoes a decomposition reaction, forming water and oxygen. Fortunately, the reaction is slow enough that your bottle will last for a few years. If you were to sprinkle in some solid manganese dioxide, however, the contents of the bottle would completely decompose in a matter of seconds. Remarkably, *all* of the manganese dioxide could be filtered off from the remaining water and reused to speed the decomposition of another bottle of hydrogen peroxide. Substances such as manganese dioxide, which speed up a chemical reaction without being consumed in the reaction, are called *catalysts*.

The process of life itself depends on catalytic molecules known as *enzymes*. Most biochemical reactions rely on enzymes which increase the rate of the reaction by 1,000 to 100,000,000,000,000,000 times when compared with the uncatalyzed reaction. An even more remarkable property of enzymes is that they produce reaction products at near-100% yields, allowing all of the reaction energy to be used by the cell as well as virtually eliminating any undesirable by-products.

No matter the type of chemical change that you may consider—burning, rusting, decomposition, biological reactions, or any other transformation—you can see that an understanding of the reaction kinetics is essential to comprehending the process.

Average and Instantaneous Rate

You arrive at school one day, and as you wait for your first class to begin, your friend arrives, sits next to you, and remarks, "It was a slow commute today." You ask, "How fast did you travel?" Your friend looks back at you with a puzzled look in her eyes.

How do you respond to someone who asks about the speed of a trip? If the distance from home to school is ten miles and it takes a half hour to make the trip, your average speed, or *average rate* of travel, is 20 miles per hour. However, along the way you may have gone as fast as 45 mph, but at other times you were stopped. Your speed at any given instant, your *instantaneous rate*, is shown by your speedometer reading at that moment. Clearly, there are two ways of expressing rates, your choice of which depends on the type of information that is needed.

The rate of a chemical reaction is defined as the change in concentration of a reactant or product of that reaction per unit time. This can be expressed as $\frac{\Delta C}{\Delta t}$. Just as with the speed of a trip from home to school, chemical reaction rates can be average or instantaneous. To obtain an instantaneous rate, the reaction needs to be examined over a time period small enough to ensure that the reaction has proceeded only slightly.

If we experimentally measure how the rate of a chemical reaction depends on the concentrations of the reactants or products, we can develop what is known as a rate law or a rate expression for that particular reaction. With the rate expression we can predict how concentrations will affect the reaction. We can also use the rate expression as a piece of evidence in the construction of an understanding about how the reaction takes place at the particulate level. This description of the particulate-level steps in a reaction is called a reaction mechanism. In this workshop you will learn how to interpret experimental rate data and find the rate expression.

Rate Expressions / Rate Laws

Many reactions have an instantaneous rate expression that follows the general form

$$\text{rate} = k\,[\text{reactant 1}]^m\,[\text{reactant 2}]^n \ldots.\text{etc.}$$

where k is the proportionality constant that relates the rate or speed at which the reaction occurs to the concentrations of reactants or products. The concentration of each species in the reaction is modified by an exponent: m and n in this general case. These exponents are known as the *order* of the reaction with respect to each species in the reaction. We would say that the reaction is of m order in reactant 1, n order in reactant 2, etc. The sum of the exponents is known as the overall reaction order.

Let's consider the simple reaction A ➔ B and look at some common types of differential rate expressions. A *rate law* or *rate expression* describe how the reaction speed depends on the concentrations of reactants or products (most often reactants). It is determined from experiments that measure the change in concentration of one or more of the reactants or products over time. Consider the following rate laws that can apply to the general reaction A + B ➔ Products:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A] \qquad \textbf{(Eq. 1)}$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]^2 \qquad \textbf{(Eq. 2)}$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]\,[B] \qquad \textbf{(Eq. 3)}$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k \qquad \textbf{(Eq. 4)}$$

Equations Eq. 1–4 express the rate of the reaction in terms of the disappearance of A, rate $= \frac{\Delta[A]}{\Delta t}$. This rate is proportional to the molar concentration of A and/or B, raised to a power. In each case, the proportionality constant is given by k, which is known as the *rate constant.*

The term *reaction order* is used to refer to the exponents of the concentrations. We can refer to the overall reaction order, the sum of the exponents of all of the reactants, or the reaction order of a particular reactant, the exponent of that reactant. For example, the rate law in Equation Eq. 2 is said to be second order with respect to A. For Equation Eq. 3, the reaction is second order overall and first order for each of the reactants. It is important to note that the order of the reaction does not necessarily follow from the reaction stoichiometry.

The rate laws we have seen so far express the relationship between rate and concentration. Another form for expressing rate laws is to show the relationship between concentration and time. These are called **integrated rate laws**. The chart below shows the differential rate law, the type we first introduced, and the corresponding integrated rate law for zeroth, first, and second order reactions.

Differential RateLaws / Expressions	*Integrated Rate Laws / Expressions*
$\text{rate} = -k$	$[A] = [A]_0 - kt$
$\text{rate} = -k\,[A]$	$[A] = [A]_0 \times e^{-kt}$
$\text{rate} = -k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Differential Rate Expressions:

First Order

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]$$

This expression tells us that the rate of the reaction is equal to the opposite of the change in the concentration of A per change in time, and this is also equal to a constant, k, times the concentration of A. The constant k is known as the *rate constant*. The concentration unit is molarity, as implied by the square brackets. A reaction rate is expressed as a positive number. Since the concentration of A is decreasing, $\Delta[A]$ is negative. The minus sign preceding the expression makes the rate net positive. This reaction is first order in A and overall first order.

Let's step back from all of the vocabulary and formalism for a moment and think about what this rate law really tells us. Essentially, it says that the speed at which the reaction proceeds is equal to a proportionality constant times concentration of A. Given that k is a constant, the only variable in this equation that will affect the reaction rate is the concentration of the reactant. Reaction rate can be measured by following the change in the concentration of the reactant, A, per change in time. The rate varies as the concentration varies. If the concentration of A is doubled, the reaction proceeds twice as fast.

Second Order

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

Here the reaction is second order with respect to the concentration of A and second order overall. If the concentration of A is doubled, the reaction will proceed four times as fast.

Half Order

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]^{1/2}$$

This reaction is one-half order with respect to A and overall. If the concentration of A is doubled, the reaction rate will increase by a factor of $(2)^{1/2}$, or $\sqrt{2}$, which is 1.4.

Zero Order

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k$$

Here the rate of the reaction does not depend on the concentration of A.

Instantaneous rates are determined experimentally by the application of a technique known as the method of initial rates. The initial instantaneous rate of reaction is approximated by measuring the change in concentration in the smallest time interval practical. This provides a good approximation to the instantaneous rate:

$$\frac{\Delta[A]}{\Delta t} = \frac{[A]_{t=1} - [A]_{t=0}}{t_1 - t_0}$$

We can measure the initial rate for different initial concentrations of each of the reactants, and from those data, find the rate order. The value of the rate constant follows because now we know the initial rate, the initial concentrations, and the rate orders for each reactant.

Integrated Rate Expressions:
The differential rate law relates the reaction rate and concentrations. Many times it is more important to understand how concentration changes as a function of time, and this relationship is given by what is known as the integrated rate law.

First Order

$$[A]_t = [A]_{t=0}\, e^{-kt} \quad \textit{or} \quad \ln [A]_t = -kt + [A]_{t=0}$$

Second Order

$$\frac{1}{[A]_t} = \frac{1}{[A]_{t=0}} + kt$$

Integrated rate expressions are used are often applied to the problem of determining the order of a chemical reaction. From the first order rate law, you can see that a graph of ln [A] vs. t will result in a straight line with a slope of –k and a y-intercept of $[A]_{t=0}$.

Reaction half-life:
The rate constant can be expressed in an alternate form known as the *half-life* of the reaction, which is defined as the time needed for the reactant concentration to fall to exactly half of its original concentration. Half-lives are most commonly used for first-order reactions. The relationship between the half-life and the rate constant for a first-order reaction is given by

$$t_{1/2} = \ln 2 / k \qquad \textbf{(Eq. 5)}$$

Reversibility:
It is often the case that the rate of reaction will depend not only on the reactant concentrations but also the product concentrations as well. For example, the experimentally-determined rate law for the reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

may be

$$\text{rate} = -k_1 [A] + k_{-1} [B] \qquad \textbf{(Eq. 6)}$$

In this case, the reaction is said to be *reversible*. You will see that kinetic reversibility is closely connected with the concept of equilibrium

The Arrhenius Equation:

The Swedish chemist Svante Arrhenius was the first to note that the rate constant for many chemical reactions increased with temperature. He formulated a mathematical expression of this relationship, and it is now known as the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where A is known as the frequency (or preexponential) factor and E_a is the activation energy. The frequency factor is the value of the rate constant if all molecular collisions were successful reaction-producing collisions. The activation energy is the energy barrier that must be overcome for a reaction to occur. The complete exponential term gives the fraction of reactant molecules that have sufficient energy to overcome the energy barrier.

For a reaction that obeys the Arrhenius equation, a graph of ln k versus 1/T has a slope of $-E_a/R$ and an intercept of ln A.