**Basics**

Suppose I have a chemical reaction:

$$A + B \rightarrow C + D$$

The extent of the reaction is described by the amount of the substance that has reacted. One basic unit for this measurement is *moles* ($m$). The measure used in practice is *moles per unit volume* ($M$). This is called concentration and the notation is $[A]$.

The rate of the reaction depends upon the conditions under which the reaction occurs, such as temperature, pressure, and concentrations of some of the substances present. It is important to know both the rate and the extent of the reaction at the same time. The rate of a reaction is the derivative of the extent of the reaction. (One way to know both at the same time is to measure the initial rate of the reaction.)

The rate of the reaction is usually written in terms of the rate of consumption of the reactants. In other words, the rate is a function of the reactant concentrations. The nature of this function is known: the rate of a reaction is directly proportional to the concentrations of one or more of the reactants raised to some power as long as the temperature and other environmental variables are kept constant.

Mathematically, we write "the rate of the reaction = $k[A]^p[B]^q$".

Experimentally, it has been found that the powers $p$ and $q$ are often integer, but they can be negative or fractional. The values of $p$ and $q$ are called the orders of the reaction and $k$ is called the rate constant. If $p$ is 2 and $q$ is 1, then the rate law would be described as second order in $A$, first order in $B$, and 3rd order overall. Both the order of a reaction and the rate constant must be determined experimentally.

Let’s look at this mathematically. The rate of the reaction is a function of $[A]$ and $[B]$, both of which the experimenter can control: rate = $f([A],[B])$. If we fix $[B]$ and vary $[A]$, we have a single-variable function. (This is called the partial derivative of $f$ with respect to $[A]$.)

Let $x = [A]$ and $y = [B]$. Note we have been looking at rate as $f(x,y)$. But $x$ and $y$ are themselves functions of time, $x(t)$ and $y(t)$, so rate is $f(x(t),y(t))$, a function of time. What we have is the following: rate of the reaction = $kx(t)^py(t)^q$.

**The dataset.**

The dataset *chem_reaction* comes from an experiment to measure the reaction rate for the following reaction:

$$\text{(1)} \quad \text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$$

Two other (much faster) reactions:

$$\text{(2)} \quad 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$

$$\text{(3)} \quad \text{I}_2 + \text{starch} \rightarrow \text{I}_2\text{-starch} \text{ (blue-black)}$$

are used.

In a nutshell, in the lab students add a solution of $\text{I}^-, \text{S}_2\text{O}_3^{2-}$ and starch to a solution of $\text{S}_2\text{O}_8^{2-}$. The time until the blue-black color appears is recorded. In runs A-1 through A-3, the initial
concentration of \( S_2O_8^{2-} \) is kept constant and the initial concentration of \( I^- \) is varied. In runs B-1 through B-3, the initial concentration of \( S_2O_8^{2-} \) is varied and the initial concentration of \( I^- \) is kept constant. (Runs C-1 thru C-4 correspond to keeping concentrations constant and varying temperature.)

The rate of the reaction is estimated as follows. The rate of change in the reactant \( S_2O_8^{2-} \) is used for the rate of the reaction. This is computed for each run as the change in concentration of \( S_2O_8^{2-} \) divided by the change in time during the period between the start of the experiment and the time when the blue-black color appears.

The time that the blue-black color appears corresponds to time in which the initial amount of \( S_2O_3^{2-} \) is used up. (Why? The reaction described in (1) is producing \( I_2 \). The \( I_2 \) reacts with the \( S_2O_3^{2-} \) as described by (2) until the \( S_2O_3^{2-} \) is used up. Then the \( I_2 \) being produced by reaction (1) reacts with the starch as described in (3) and blue-black appears. Since the reaction (3) is fast compared to (1), the appearance of the blue-black nearly coincides with the time in which the \( S_2O_3^{2-} \) is used up.) Since two moles of \( S_2O_3^{2-} \) are used up for each mole of \( I_2 \) used and one mole of \( I_2 \) is produced per mole of \( S_2O_8^{2-} \), we have that the change in concentration of \( S_2O_8^{2-} \) is half the change in concentration of \( S_2O_3^{2-} \). The recorded time is the time until the amount of \( S_2O_3^{2-} \) is 0. The initial concentration of \( S_2O_3^{2-} \) is known. In this chemistry lab, it was \( 1.54 \times 10^{-3} \text{ M} \) (moles per unit volume), and so the change in concentration of \( S_2O_3^{2-} \) is \( 0 - 1.54 \times 10^{-3} \text{ M} \). The change in concentration of \( S_2O_8^{2-} \) is \( -(1/2) \times (1.54 \times 10^{-3}) = -7.70 \times 10^{-3} \text{ M} \). Thus, the rate of the reaction in this experiment will be computed for each run as \(-7.70 \times 10^{-3} \text{ divided by the time until blue-black color appears.}\)

It is important to note that the rate of the reaction changes as the amount of the reactants change. We estimate the reaction rate at a time at which we know the amount of the reactants present—at the beginning of the reaction. Reactions (2) and (3) are fast compared to (1) and the initial amount of \( S_2O_3^{2-} \) is purposefully kept small so that the rate computed is very close to the initial rate of the reaction.