A chemist would start a description of chemical kinetics by designing an imaginary reaction where A is converted to B:

\[ A \rightarrow B \]

You could then calculate how the concentration of A decreases and B increases as the reaction progresses. In chemistry it is relatively easy to provide examples of what A and B are (e.g., \( H_2O_2 \) reacts to form water and half a molecule of oxygen). If we are concerned with the organic chemistry going on in foods we could do something similar. For example during pasteurization vitamin C is thermally destroyed and studying the kinetics of the reaction would teach us something about how the nutritional quality of the drink would change. In another example we might be interested in how spinach loses its green color during steaming. If we know the green color of spinach is due to the pigment chlorophyll then we can use measurements of chlorophyll concentration as a chemical proxy for color. Here [chlorophyll] is not interesting in itself, but only as it tells us the color of the plant food. However, in other cases we might have no idea what chemical reaction is responsible for the changes in food quality we are interested in. For example cornflakes sometimes become soft if they are stored too long, coffee stored hot might become bitter and lose its characteristic flavor, meat roasted for long periods of time might become dry. In all of these cases we cannot point to a chemical reaction as responsible for the changes we are interested in. We can however say that some sort of reaction must have taken place and so write a general expression:

\[ \text{Reagents} \rightarrow \text{Products} \]

We can define [reagents] and [products] in whatever way is convenient or us, in the earlier chemical examples this would have been simply [vitamin C] and [chlorophyll] but in the later food examples it could be instrumental measurement of cornflake texture, sensory score of coffee quality, of change in mass of the meat roast as it dries out in the oven. The later examples are not defined chemical reactions but can be measured and will change as the reaction proceeds. We will use mathematical models to predict how food will respond to different conditions and use that to estimate a maximum shelf-life or optimum processing time.

If reagents are being converted to products then the rate of loss of one is equal to the rate of gain of the other (note Products are always shown as Positive):

\[ \frac{dR}{dt} = -\frac{dP}{dt} \]
The rate of the reaction depends on the mechanism. To illustrate this imagine we were modeling the process of bacterial growth. Simply put, to make a new bacterium the parent splits into two

\[ \text{Bacterium} \rightarrow \text{Bacterium + Bacterium} \]

Typically a bacterial like *e. coli* can do this every 30 mins. So one bacterium at time zero would lead to
- At 30 min 2 bacteria,
- At 60 min 4 bacteria
- At 90 min 8 bacteria
- At 120 min 16 bacteria
- At 150 min 32 bacteria etc.

The number of bacteria is increasing with time but so is the rate of increase. In the first 30 min the change in the number of bacteria is 1 so \( \frac{dP}{dt} = \frac{1}{30} \text{ min}^{-1} \). In the second 30 min it is \( \frac{2}{30} \text{ min}^{-1} \), then \( \frac{4}{30} \text{ min}^{-1} \) and so on. Essentially the same “reaction” is occurring but \( \frac{dP}{dt} \) is progressively increasing. We can easily show that the rate is proportional to the number of bacteria there and so

\[ \text{Rate} = k [\text{Reagents}] \]

Where \( k \) is a proportionality constant, the rate constant. We say this is a first order reaction because \([\text{Reagents}]\) is raised to the power 1 (not shown in the equation). The higher the value of \( k \) the faster the reaction proceeds. The rate constant defines the proportion of reagents that will react in a given time. The absolute numbers that react depend on how many are there.

Consider a second example. During yogurt manufacture we are interested in making the milk proteins set to form a gel. The proteins we are concerned about are caseins, which naturally form into large (~1 \( \mu \)m) clumps of many protein molecules known as casein micelles. To make yogurt, the milk is fermented with lactic acid bacteria that convert the milk lactose to lactic acid and the pH drops. When the pH gets low enough the casein micelles begin to aggregate and this is the first step in the formation of the yogurt gel. Expressed this way the reaction we are concerned with is

\[ \text{Casein micelle + casein micelle} \rightarrow \text{casein dimer} \]

The rate of the reaction is \(-d[\text{casein micelle}] / dt\) or \(d[\text{casein dimer}] / dt\). In order to react the two micelles must collide, the rate of a binary collision is proportional to concentration squared. The chance of a casein micelle hitting another casein micelle is proportional to the number of casein micelles available
i.e., Rate of a given micelle hitting another one \( \propto \) number available

But each micelle has this chance of colliding so the total number of collisions is this times the total number of micelles available:

i.e., total rate of collisions \( \propto \) number available \( \times \) number available

or \[
\text{Rate} = -d[\text{micelles}]/d (\text{time}) = -k[\text{micelles}]^2
\]

Where \( k \) is a rate constant. The order of the reaction is here 2 because it is proportional to the rate raised to the second power. Note also the unit of \( k \) depends on the order of the reaction, absolute rate is always \(<\text{concentration}> <\text{time}>^{-1}\), but the rate constant is in units \(<\text{concentration}>^{\text{order}-1} <\text{time}>^{-1}\).

Consider a third, more trivial example – the change in volume of soda in a drinks dispenser in a convenience store. We could write the change as a “reaction”

\[
\text{Soda in container} \rightarrow \text{Soda dispensed}
\]

With a rate equal to \(-d[\text{soda in container}]/d [\text{time}]\) (here we should use volume of soda in container rather than the concentration brackets “[ ]” but we will cautiously maintain the convention for consistency). We can easily measure the volume of the container and would expect a typical plot to be similar to that shown in the Figure. Note that the rate is not constant (customers either take a full cup or nothing so it appears as a stepwise function), nor are the cups poured at a regular rate, however we can see that the overall rate of decrease in volume is approximately linear with time. The change in soda volume in a given time depends on the flow of customers through the store and how thirsty they are not on how much soda is in the container. So the rate is:

\[
\text{Rate} = -d[\text{soda in container}]/d [\text{time}] = -k
\]
The rate is constant \((-k)\) and the reaction is zeroth order with respect to soda volume, i.e., the possibility of selling a soda doesn’t depend on how much is available.

Building off the logic of the previous paragraph we could hypothesize that \(k\) could be expressed as a function of the rate of customers entering the store times their average thirstiness but not on the volume of soda, i.e.,

\[ k = k' \times \text{rate of custom} \times \% \text{thirstiness} \]

So we have identified three separate formulae of the rates of reaction with different order. Combining them we can see that in general:

\[ \text{Rate} = -k[\text{reagents}]^n = k[\text{products}]^n \]

Where \(k\) is the rate constant of the reaction and \(n\) is the order \((=0-2)\). Finally consider a truly complex reaction, for example the formation of brown color on the crust of a loaf as it bakes. The color is due to pigments known as melanoidins forms from the reaction between amines (from proteins) and reducing sugars (i.e., those with a free aldehyde group). A simplified mechanism of the reaction is given in the Hodge scheme (see later in the notes for a more complete treatment of this famously complex reaction)

\[
\text{Reducing sugar + Amine} \rightarrow \text{Intermediates} \rightarrow \text{Brown pigment}
\]

But that would clearly be a gross oversimplification ignoring the potential for cross reactions, catalytic intermediates, non-pigmented products etc. In fact there are many pathways and competing reactions could lead to the colored product we are interested in and in all cases multiple reaction steps are involved, each with different rates and orders. In steady state, we can still say: \(\text{Rate} = k[\text{brown color}]^n\), where \(k\) is the rate of a composite reaction but because it is a composite reaction we need no-longer assume \(n\) has an integer value\(^1\).

The equation \(\text{Rate} = -k[\text{reagents}]^n\) is a start but not a really that helpful. It tells us that if we know two parameters (\(k\) and \(n\)) we can calculate the rate of change of something. However, rate of change is not what we need to know but rather the absolute amount as a function of time (e.g., how much vitamin C is there after 10 min cooking or how much soda will be left by the end of the day). We need to integrate the rate equation, so if

\[
\frac{dR}{dt} = \frac{dP}{dt} = k[P]^n
\]

Then:

\[
P = \int [k[P]^n \, dt
\]

\(^1\) In the context of this class we will not be concerned with non-integer reaction orders, but you should be aware that they may exist.
Starting with a trivial example, zeroth order reactions, Rate=$d[P]/dt=k$, therefore

$$P = \int_{t} k \, dt = kt$$

or $[R]=[R_0]-kt$, where $R_0$ is the starting concentration of reagents. So in the soda example if we know $k$ is 10 l hr$^{-1}$, we can say that after 2 hours 20 liters of soda will have been dispensed.

Life gets slightly more complicated for the higher order reactions. For the first order case Rate=$d[R]/dt=-k[R]$ so

$$\int_{R}^{R_0} \frac{1}{R} \, dR = -\int k \, dt$$

$$\ln(R) + C = -kt$$

where $C$ is an integration constant. Knowing that at time zero, $R$ is at a maximum starting value ($=R_0$) we can say:

$$\ln(R_0) + C = -k \times 0$$

$$C = -\ln(R_0)$$

substituting:

$$-\ln \left( \frac{R}{R_0} \right) = kt$$

$$R = R_0 \exp(-kt)$$

This equation implies that the logarithm of the relative extent of the reaction ($R/R_0$) should be proportional to time. This is easy to verify graphically. There are also standard integrals for second order and non-integer reactions (see Table 1 on page 1018 of the Fennema text). Once we know order and rate constant we can use these equations to calculate concentration as a function of time.

From the form of the equations we can see that a plot of $[R]$ with time should give a straight line when plotted against time only for a zeroth order reaction, $\ln (R/R_0)$ should give a straight line for a first order reaction. By plotting our data in this manner we can identify the order of the reaction (which plot gives the best straight line) and the rate constant (what is the slope of the straight line plot).
3. Temperature Dependency

The rate of chemical reaction depends on the conditions (e.g., temperature, pH, presence of catalysts or inhibitors). It would be helpful to incorporate these terms into our rate equations so we could extend them to conditions other than those where measurements were made. The most successful and general approach to this problem is the use of Arrhenius kinetics which relate the rate constant to temperature:

\[ k = k_0 \exp\left(\frac{-E_a}{RT}\right) \]

where \( k \) is the rate at absolute temperature \( T \), \( E_a \) is the activation energy of the reaction (a measure of how much faster the reaction goes when heated), \( R \) is the gas constant (≈8.3 J K\(^{-1}\) mol\(^{-1}\)), and \( k_0 \) a constant (the rate at a reference temperature). This equation tells us that as \( T \) increases, the term in brackets decreases, so the left hand side of the equation increases, so the right hand side of the equation increases. Meaning as temperature increases so does the reaction rate – the equation makes qualitative sense. It is easier to deal with an equation containing an exponential by taking logs and turning it into a linear expression. In this case taking the natural log of both sides:

\[ \ln k = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T} \]

Compare this equation to the equation of a straight line, \( y=C-Mx \). If we plot \( \ln k \) against \( 1/T \) we would expect a straight line with \( y \)-intercept of \( k_0 \) and a slope of \( -E_a/R \). It is then possible to calculate the constants by fitting a best-fit line to the data and then calculate the rate constant at any temperature. Knowing the rate constant and assuming the order of the reaction is unchanged by the change in temperature the progression of the reaction at a different temperature can then be calculated using one of the rate equations developed earlier.