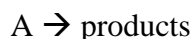


Chapter 12: Chemical Kinetics II – Mechanisms

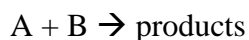
In the previous chapter, we discussed the rates of chemical reactions. In this chapter, we will expand on the concepts of chemical reaction rates by exploring what the rate law implies about the mechanistic pathways that reactions actually follow to proceed from reactants to products. Typically, one determines a rate law that describes a chemical reaction, and then suggests a mechanism that can be (or might not be!) consistent with the observed kinetics. This chapter will be concerned with reconciling reaction mechanisms with predicted rate laws.

Reaction Mechanisms

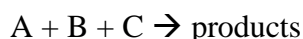
A **reaction mechanism** is a set of **elementary reactions** steps, that when taken in aggregate define a chemical pathway that connects reactants to products. An elementary reaction is one that proceeds by a single process, such a molecular (or atomic) decomposition or a molecular collision. Typically, elementary reactions only come in **unimolecular**



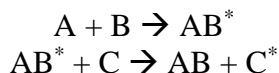
and **bimolecular**



form. Occasionally, an elementary step that is **termolecular**



(involved the simultaneous collision of three atoms or molecules) but it is generally a pair of bimolecular steps acting in rapid succession, the first forming an activated complex, and the second stabilizing that complex chemically or physically.



The wonderful property of elementary reactions is that the **molecularity** defines the order of the rate law for the reaction step.

The Requirements of a Reaction Mechanism

A valid reaction mechanism must satisfy three important criteria:

1. The sum of the steps must yield the overall stoichiometry of the reaction.
2. The mechanism must be consistent with the observed kinetics for the overall reaction.

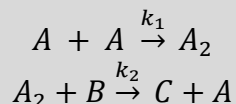
- The mechanism must account for the possibility of any observed side products formed in the reaction.

Example:

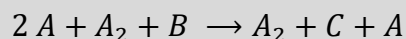
For the reaction



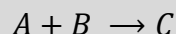
is the following proposed mechanism valid?

**Solution:**

Adding the reactions gives



Canceling those species that appear on both sides of the arrow leaves



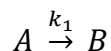
which is the reaction, so the mechanism is at least stoichiometrically valid. However, it would still have to be consistent with the observed kinetics for the reaction and account for any side-products that are observed.

Concentration Profiles for Some Simple Mechanisms

To illustrate how mechanisms may affect the concentration profile for a reaction, we can examine some simple mechanisms

$A \rightarrow B$

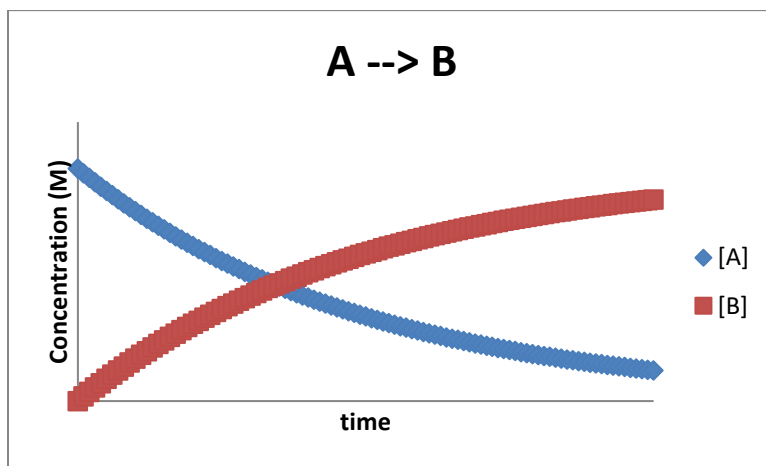
In this type of reaction, one substance is simply converting into another. An example of this type of reaction might be the isomerization of methylisocyanide to form acetonitrile (methylcyanide) (Redmon, Purvis, & Bartlett, 1978). If the reaction mechanism consists of a single unimolecular step, which is characterized by the rate constant k_1



then rate of change of the concentrations of A and B may be written

$$\frac{d[A]}{dt} = -k_1[A] \quad \text{and} \quad \frac{d[B]}{dt} = k_1[A]$$

A plot the concentrations as a function of time would look as follows:



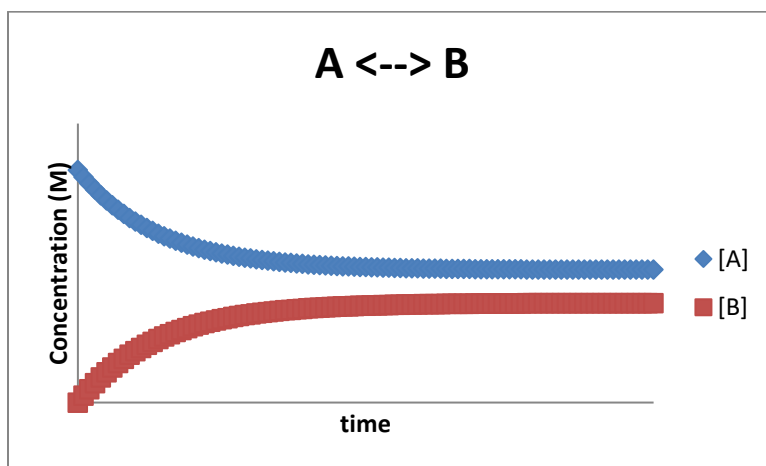
It can be easily seen that the concentration of the reactant (A) decreases as time moves forward, and that of the product (B) increases. This will continue until reactant A is depleted.

$A \rightleftharpoons B$

When the system can establish equilibrium, the rate of change of the concentration of A and B will depend on both the forward and reverse reactions. If k_1 is the rate constant that characterizes the forward reaction, and k_{-1} that which characterizes the reverse, then

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \quad \text{and} \quad \frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

The concentration profile for this situation looks as follows:



This profile is characterized by the fact that after a certain amount of time, the system achieves equilibrium and the concentrations stop changing (even though the forward and reverse reactions are still taking place. This is the nature of a **dynamic equilibrium** about which we speak off of the time in chemistry. The final concentrations of [A] and [B] once equilibrium is established will depend on the ratio of k_1 and k_{-1} . The rate of change on concentrations of A and B can be expressed

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

Since the rate of formation of A (from the reverse step) is equal to the rate of consumption of A (from the forward step, the overall rate of change of the concentration of A is zero once equilibrium has been established. So it should be clear that

$$k_1[A] = k_{-1}[B]$$

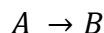
or

$$\frac{k_1}{k_{-1}} = \frac{[B]}{[A]}$$

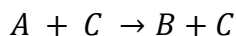
and the ratio $\frac{k_1}{k_{-1}}$ gives the value of the equilibrium constant!

$A + C \rightarrow B + C$

Some reactions require a **catalyst** to mediate the conversion of reactants in to products. The definition of a catalyst is a species that must be added (it is not formed as an intermediate) shows up in the mechanism (usually in a very early step) and this ends up as part of the rate law, but is reformed later on so that it does not appear in the overall stoichiometry. If the reaction



is aided by a catalyst C, then one possible reaction mechanism might be

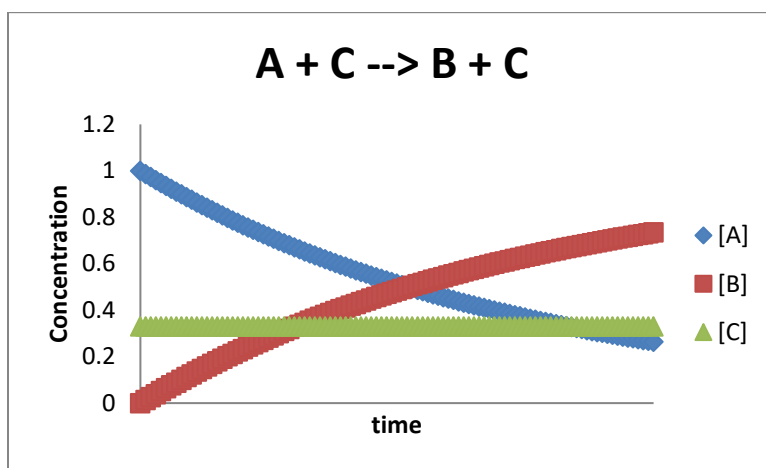


In this case, C is acting as a catalyst to the reaction. The rate of change of the concentrations can be found by

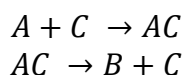
$$\frac{d[A]}{dt} = -k[A][C]$$

$$\frac{d[B]}{dt} = k[A][C]$$

$$\frac{d[C]}{dt} = -k[A][C] + k[A][C] = 0$$



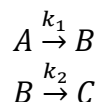
This is a very simplified picture of a catalyzed reaction. Generally a catalyzed reaction will require at least two steps:



Later, we will see how the steady-state approximation actually predicts the above depicted concentration profile for the two-step mechanism when AC is a short-lived species that can be treated as having a constant and small concentration.



Another important (and very common) mechanistic feature is the formation of an intermediate. This is a species that is formed in at least one of the mechanism step, but does not appear in the overall stoichiometry for the reaction. This is different from a catalyst which must be added to speed the reaction. A simple example of a reaction mechanism involving the formation of a catalyst is



In this case, C cannot form until an appreciable concentration of the intermediate B has been created by the first step of the mechanism.

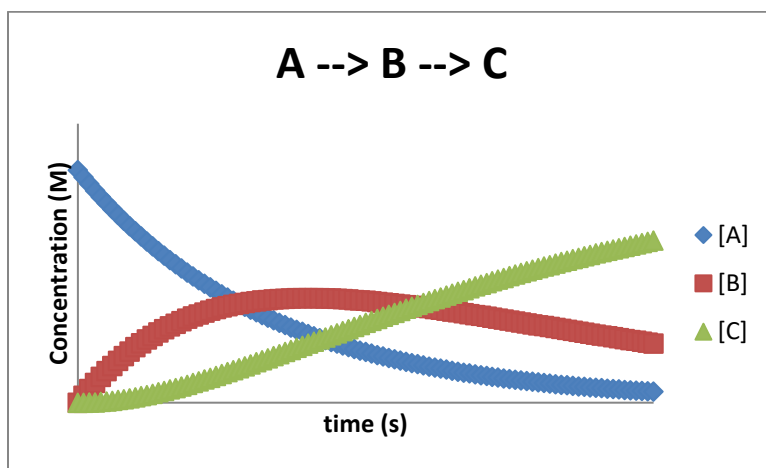
The rate of change of the concentrations of A, B, and C can be expressed

$$\frac{d[A]}{dt} = -k_1[A]$$

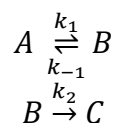
$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

The concentration profile is then shown below. Notice the delay in the formation of C.



In many cases, the formation of an intermediate involves a reversible step. This step is sometimes referred to as a **pre-equilibrium** step since it oftentimes will establish a near equilibrium while the reaction progresses. The result of combining a pre-equilibrium with an intermediate produces a profile that shows features of both of the simpler mechanisms. An example of such a mechanism is



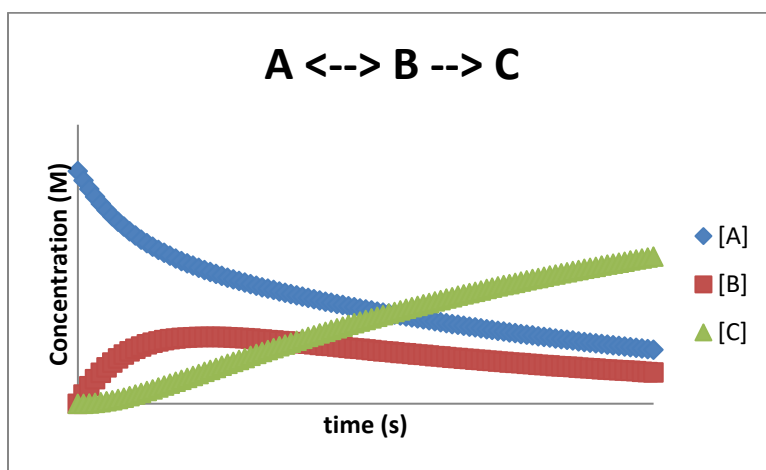
In this case, the rate of change for the concentrations of A, B, and C can be expressed by

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

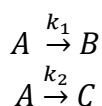
$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

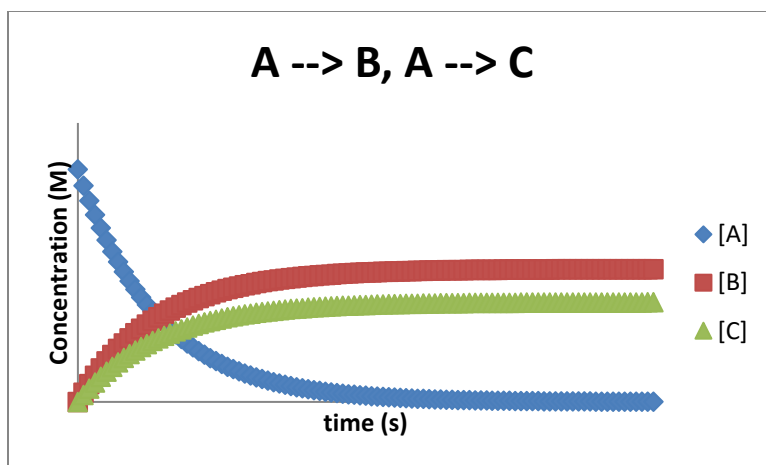
$$\frac{d[C]}{dt} = k_2[B]$$

The concentration profile for this mechanism is shown below. Again, notice the delay in the production of the product C, due to the requirement that the concentration of B be sufficiently high to allow the second step to occur with an appreciable rate.



There are many cases where a reactant can follow pathways to different products (or sometimes even the same products!), and those pathways compete with one another. An example is the following simple mechanism:





In this case, the rate of change on concentrations can be expressed as

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\frac{d[B]}{dt} = k_1[A]$$

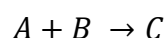
$$\frac{d[C]}{dt} = k_2[A]$$

Overall, the profile looks like two first order decompositions occurring at the same time, with the final concentration of the product formed with the larger rate constant being favored.

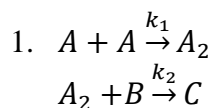
One of the goals of studying chemical kinetics is to understand how to alter reaction condition to favor the production of desirable reaction products. This can be accomplished by a number of means, such as alteration of concentrations, temperature, addition of catalysts, etc. Understanding the basics will (hopefully) lead to a better understanding of how concentration profiles can be altered by changing conditions.

The Connection between Reaction Mechanisms and Reaction Rate Laws

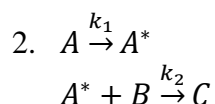
The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction



might be proposed to follow one of two mechanistic pathways:



or

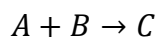


The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

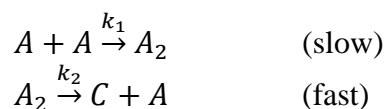
In order to analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on the **Rate Determining Step** approximation, the **Steady State** approximation, and the **Equilibrium** approximation. Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

The Rate Determining Step Approximation

The **rate determining step** approximation is one of the simplest approximations one can make to analyze a proposed mechanism to deduce the rate law it predicts. Simply stated, the rate determining step approximation says that a mechanism can proceed no faster than its slowest step. So, for example, if the reaction



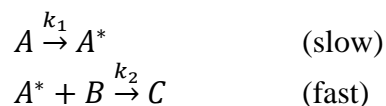
is proposed to follow the mechanism



the rate determining step approximation suggests that the rate (expressed in terms of the appearance of product C) should be determined by the slow initial step, and so the rate law will be

$$\frac{d[C]}{dt} = k_1[A]^2$$

matching the order of the rate law to the molecularity of the slow step. Conversely, if the reaction mechanism is proposed as



the rate determining step approximation suggests that the rate of the reaction should be

$$\frac{d[C]}{dt} = k_1[A]$$

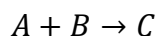
again, with the order of the rate law matching the molecularity of the rate determining step.

The Steady-State Approximation

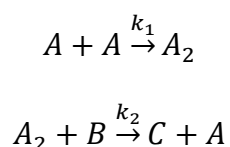
One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction



is proposed to follow the mechanism



The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$0 = k_1[A]^2 - k_2[A_2][B]$$

or

$$[A_2] = \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

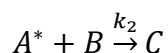
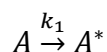
the above expression for $[A_2]$ can be substituted:

$$\frac{d[C]}{dt} = k_2 \left(\frac{k_1[A]^2}{k_2[B]} \right) [B]$$

or

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$. On the other hand, if the mechanism is proposed to be



then the rate of change of the concentration of A^* is

$$\frac{d[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds $\left(\frac{d[A^*]}{dt} = 0 \right)$ then

$$[A^*] = \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] = k_2 \left(\frac{k_1[A]}{k_2[B]} \right) [B]$$

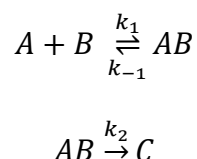
or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

The Equilibrium Approximation

In many cases, the formation of a reactive intermediate (or even a longer lived intermediate) involves a reversible step. This is the case if the intermediate can decompose to reform reactants with a significant probability as well as moving on to form products. In many cases, this will lead to a pre-equilibrium condition in which the **equilibrium approximation** can be applied. An example of a reaction mechanism of this sort is



Given this mechanism, the application of the steady state approximation is cumbersome. However, if the initial step is assumed to achieve equilibrium, an expression can be found for [AB]. In order to derive this expression, one assumes that the rate of the forward reaction is equal to the rate of the reverse reaction for the initial step in the mechanism.

$$k_1[A][B] = k_{-1}[AB]$$

Or

$$\frac{k_1[A][B]}{k_{-1}} = [AB]$$

This expression can be substituted into an expression for the rate of formation of the product C:

$$\frac{d[C]}{dt} = k_2[AB]$$

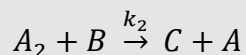
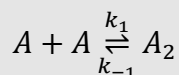
Or

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} [A][B]$$

Which predicts a reaction rate law that is first order in A, first order in B, and second order overall.

Example:

Given the following mechanism, apply the equilibrium approximation to the first step to predict the rate law suggested by the mechanism.

**Solution:**

If the equilibrium approximation is valid for the first step,

$$k_1[A]^2 = k_{-1}[A_2]$$

Or

$$\frac{k_1[A]^2}{k_{-1}} = [A_2]$$

Plugging this into the rate equation for the second step

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

yields

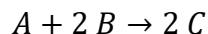
$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} [A]^2 [B]$$

Thus, the rate law has the form

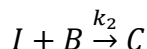
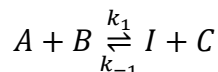
$$rate = k[A]^2[B]$$

which is second order in A, first order in B and third order over all, and in which $k = \frac{k_2 k_1}{k_{-1}}$.

Sometimes, the equilibrium approximation can suggest rate laws that have negative orders with respect to certain species. For example, consider the following reaction



A proposed mechanism for which might be



in which I is an intermediate. Applying the equilibrium approximation to the first step yields

$$k_1[A][B] = k_{-1}[I][C]$$

or

$$\frac{k_1[A][B]}{k_{-1}[C]} = [I]$$

Substituting this into an expression for the rate of formation of C, one sees

$$\frac{d[C]}{dt} = k_2 \left(\frac{k_1[A][B]}{k_{-1}[C]} \right) [B]$$

or

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} \frac{[A][B]^2}{[C]}$$

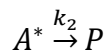
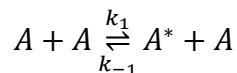
The rate law is then of the form

$$rate = k \frac{[A][B]^2}{[C]}$$

which is first order in A, second order in B, negative one order in C, and second order overall. Also, $k = \frac{k_2 k_1}{k_{-1}}$. In this case, the negative order in C means that a buildup of compound C will cause the reaction to slow. These sort of rate laws are not uncommon for reactions with a reversible initial step that forms some of the eventual reaction product.

The Lindemann Mechanism

The **Lindemann mechanism** (Lindemann, Arrhenius, Langmuir, Dhar, Perrin, & Lewis, 1922) is a useful one to demonstrate some of the techniques we use for relating chemical mechanisms to rate laws. In this mechanism, a reactant is collisionally activated to a highly energetic form that can then go on to react to form products.



If the steady state approximation is applied to the intermediate A^*

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$$

an expression can be derived for $[A^*]$.

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

Substituting this into an expression for the rate of the production of the product P

$$\frac{d[P]}{dt} = k_2[A^*]$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$$

In the limit that $k_{-1}[A] \gg k_2$, the rate law becomes first order in $[A]$.

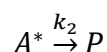
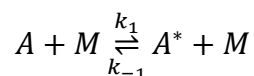
$$\frac{d[P]}{dt} = \frac{k_2 k_1}{k_{-1}} [A]$$

This will happen if the second step is very slow, such that the reverse of the first step “wins” in the competition for $[A^*]$. But in the other limit, that $k_2 \gg k_{-1}[A]$, the reaction becomes second order in $[A]$.

$$\frac{d[P]}{dt} = k_1[A]^2$$

which is consistent with the forward reaction of the first step being the rate determining step, since A^* is removed from the reaction (through the formation of products) very quickly as soon as it is formed.

Sometimes, the **third-body collision** is provided by an inert species M, perhaps by filling the reaction chamber with a heavy non-reactive species, such as Ar. In this case, the mechanism becomes



And in the limit that $[A^*]$ can be treated using the steady state approximation, the rate of production of the product becomes

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} [A]$$

And if the concentration of the third body collider is constant, it is convenient to define an **effect rate constant**, k_{uni} .

$$k_{uni} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2}$$

The utility is that important information about the individual step rate constants can be extracted by plotting $1/k_{uni}$ as a function of $1/[M]$.

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_2 k_1} + k_2 \left(\frac{1}{[M]} \right)$$

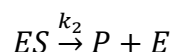
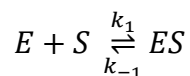
The plot should yield a straight line, the slope of which gives the value of k_2 , and the intercept gives $(k_{-1}/k_2 k_1)$.

The Michaelis-Menten Mechanism

The **Michaelis-Menten** mechanism (Michaelis & Menten, 1913) is one which many enzyme mitigated reactions follow. The basic mechanism involves an enzyme (E, a biological catalyst) and a substrate (S) which must connect to form an enzyme-substrate complex (ES) in order for the substrate to be degraded (or augmented) to form a product (P). The overall reaction is



And the simple two-step mechanism is given by



Notice that the enzyme is necessary for the reaction to proceed, but is not part of the overall stoichiometry (as is the case for any catalyst!) Applying the equilibrium approximation to the first step

$$k_1[E][S] = k_{-1}[ES]$$

And using a mass conservation relationship on the enzyme (noting that the enzyme must be either in its bare form (E) or complexed with a substrate (ES)),

$$[E]_0 = [E] + [ES] \quad \text{or} \quad [E] = [E]_0 - [ES]$$

Substituting this into the equilibrium expression yields

$$k_1([E]_0 - [ES])[S] = k_{-1}[ES]$$

Solving this expression for [ES] stepwise reveals

$$k_1[E]_0[S] - k_1[ES][S] = k_{-1}[ES]$$

$$\begin{aligned} k_1[E]_0[S] &= k_1[ES][S] + k_{-1}[ES] \\ &= (k_1[S] + k_{-1})[ES] \end{aligned}$$

$$\frac{k_1[E]_0[S]}{k_1[S] + k_{-1}} = [ES]$$

Substituting this into the expression for the rate of production of the product P

$$\frac{d[P]}{dt} = k_2[ES]$$

yields

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [E]_0 [S]}{k_1 [S] + k_{-1}}$$

Multiplying the top and bottom of the expression on the right hand side by $1/k_1$ gives the result

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{[S] + \frac{k_{-1}}{k_1}}$$

The ratio of k_{-1}/k_1 is the equilibrium constant that describes the dissociation of the enzyme-substrate complex, K_d . Noting that $k_2[E]_0$ gives the maximum rate (V_{\max})¹, and that $\frac{d[P]}{dt}$ is the reaction rate, the rate law takes the form

$$rate = \frac{V_{\max}[S]}{K_d + [S]}$$

In the limit that the substrate concentration is large compared to K_d , the reaction ends up zeroth order. This is characteristic of a bottleneck in the mechanism, which would happen if there is a shortage of enzyme sites to which the substrate can attach. In the other extreme, in which K_d is very large compared to the substrate concentration, the reaction become first order in substrate.

In an alternate derivation (Briggs & Haldane, 1925) using the steady state approximation applied to the enzyme-substrate complex

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

Solving for $[ES]$ gives the result

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

or

$$[ES] = \frac{[E][S]}{K_M}$$

where

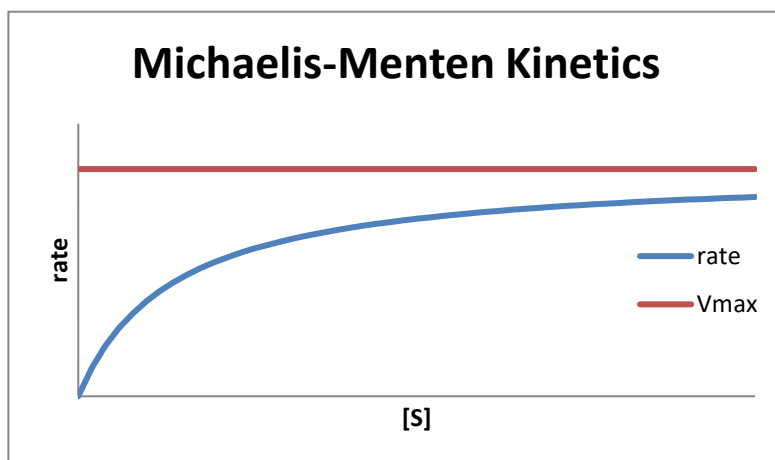
$$K_M = \frac{k_{-1} + k_2}{k_1}$$

¹ This is because the maximum reaction rate is achieved when $[ES]$ is low. As $[ES]$ increases, the likelihood of the complex decomposing to reform reactants is higher, slowing the conversion. $[ES]$ will be low if the concentration of the enzyme is much larger than that of the substrate, so there is never a shortage of enzyme available to form the complex with the substrate. However, if the substrate concentration is higher, the lack of available enzyme active sites will slow the reaction and cause it to become 0th order.

K_M is the **Michaelis constant**, which is affected by a number of factors, including pH, temperature, and the nature of the substrate itself. Proceeding as before, though the conservation of mass relationship and substitution into the expression for $\frac{d[P]}{dt}$ results in

$$rate = \frac{V_{max}[S]}{K_M + [S]}$$

The advantage to this approach is that it accounts for the loss of ES complex due to the production of products as well as the decomposition to reform the reactants E and S. As before, in the limit that $[S] \gg K_M$, the reaction reaches its maximum rate (V_{max}) and becomes independent of any concentrations. However in the limit that $[S] \ll K_M$, the reaction becomes 1st order in $[S]$.



The Michaelis constant and V_{max} parameters can be extracted in a number of ways. In the Lineweaver-Burk (Lineweaver & Burk, 1934) method, the reciprocal of the rate law is used to create a linear relationship.

$$\frac{1}{rate} = \frac{K_M + [S]}{V_{max}[S]}$$

or

$$\frac{1}{rate} = \frac{K_M}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$$

So a plot of $1/rate$ as a function of $1/[S]$ results in a straight line, the slope of which is equal to K_M/V_{max} and the intercept is $1/V_{max}$.

Chain Reactions

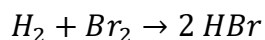
A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

initiation step – a step that creates the intermediates from stable species

propagation step – a step that consumes an intermediate, but creates a new one

termination step – a step that consumes intermediates without creating new ones

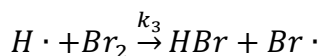
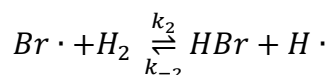
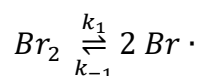
These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction



The observed rate law for this reaction is

$$rate = \frac{k[H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + k'[HBr]}$$

A proposed mechanism is



Based on this mechanism, the rate of change of concentrations for the intermediates ($H \cdot$ and $Br \cdot$) can be written, and the steady state approximation applied.

$$\frac{d[H \cdot]}{dt} = k_2[Br \cdot][H_2] - k_{-2}[HBr][H \cdot] - k_3[H \cdot][Br_2] = 0$$

$$\frac{d[Br \cdot]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br \cdot]^2 - k_2[Br \cdot][H_2] + k_{-2}[HBr][H \cdot] + k_3[H \cdot][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2 , k_{-2} , and k_3 . The result is

$$2k_1[Br_2] - 2k_{-1}[Br \cdot]^2 = 0$$

Solving for $[Br \cdot]$

$$[Br \cdot] = \left(\frac{k_1[Br_2]}{k_{-1}} \right)^{\frac{1}{2}}$$

This can be substituted into an expression for the $[H \cdot]$ that is generated by solving the steady state expression for $d[H \cdot]/dt$.

$$[H \cdot] = \frac{k_2[Br \cdot][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

So

$$[H \cdot] = \frac{k_2 \left(\frac{k_1[Br_2]}{k_{-1}} \right)^{\frac{1}{2}} [H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $[H \cdot]$ and $[Br \cdot]$, we can substitute them into an expression for the rate of production of the product HBr.

$$\frac{d[HBr]}{dt} = k_2[Br \cdot][H_2] + k_3[H \cdot][Br_2] - k_{-2}[H \cdot][HBr]$$

After substitution and simplification, the result is

$$\frac{d[HBr]}{dt} = \frac{2k_2 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [H_2][Br_2]^{\frac{1}{2}}}{1 + \frac{k_{-2}}{k_3} \frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

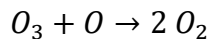
$$\frac{d[HBr]}{dt} = \frac{2k_2 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} [H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + \frac{k_{-2}}{k_3} [HBr]}$$

which matches the form of the rate law found experimentally! (Can you believe it?) In this case,

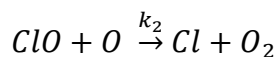
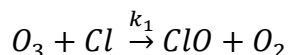
$$k = 2k_2 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} \quad \text{and} \quad k' = \frac{k_{-2}}{k_3}$$

Catalysis

There are many examples of reactions that involve catalysis. One that is of current importance to the chemistry of the environment is the catalytic decomposition of ozone (Fahey, 2006). The overall reaction



can be catalyzed by atomic chlorine by the following mechanism.



The rate of change of the intermediate (ClO) concentration is given by

$$\frac{d[ClO]}{dt} = k_1[O_3][Cl] - k_2[ClO][O]$$

Applying the steady state approximation to this relationship and solving for [ClO] produces

$$[ClO] = \frac{k_1[O_3][Cl]}{k_2[O]}$$

The rate of production of O_2 (which is two times the rate of the reaction) is given by

$$\frac{d[O_2]}{dt} = k_1[O_3][Cl] + k_2[ClO][O]$$

Substituting the expression for [ClO] into the above expression yields

$$\begin{aligned} \frac{d[O_2]}{dt} &= k_1[O_3][Cl] + k_2 \left(\frac{k_1[O_3][Cl]}{k_2[O]} \right) [O] \\ &= k_1[O_3][Cl] + k_1[O_3][Cl] \\ &= 2k_1[O_3][Cl] \end{aligned}$$

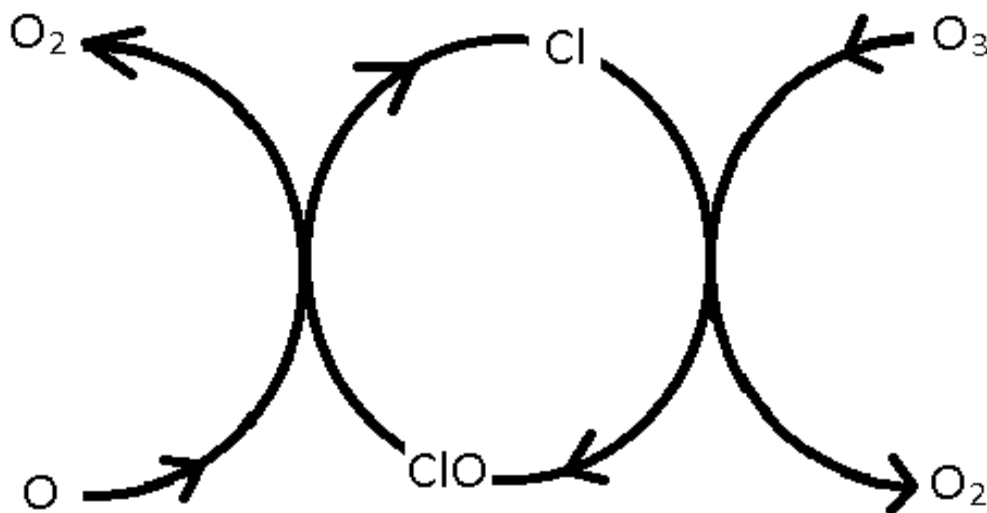
And so the rate of the reaction is predicted to be first order in $[O_3]$, first order in the catalyst $[Cl]$, and second order overall.

$$rate = k[O_3][Cl]$$

If the concentration of the catalyst is constant, the reaction kinetics will reduce to first order.

$$rate = k[O_3]$$

This catalytic cycle can be represented in the following diagram:



On the left, atomic oxygen picks up an oxygen atom from ClO to form O_2 and generate a Cl atom, which can then react with O_3 to form ClO and an O_2 molecule. The closed loop in the middle is characteristic of the catalytic cycle involving Cl and ClO . Further, since Cl acts as a catalyst, it can decompose many O_3 molecules without being degraded through side reactions.

The introduction of chlorine atoms into the upper atmosphere is a major environmental problem, leading to the annual thinning and eventual opening of the ozone layer over Antarctica. The source of chlorine is from the decomposition of chlorofluorocarbons which are used as refrigerants and propellants due to their incredible stability near the Earth's surface. However, in the upper atmosphere, these compounds are subjected to ultraviolet radiation emitted by the sun and decompose to form the radicals responsible for the catalytic decomposition of ozone. The world community addressed this issue by drafting the **Montreal Protocol** (Secretariat, 2015), which focused on the emission of ozone-destroying compounds. The result of this action has brought about evidence of the Antarctic ozone hole healing (K, 2015). This is one very good example science-guided political, industrial, and economic policies leading to positive changes for our environment.

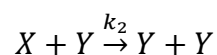
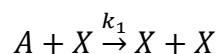
Oscillating Reactions

In most cases, the conversion of reactants into products is a fairly smooth process, in that the concentrations of the reactants decrease in a regular manner, and those of the products increase in a similar regular manner. However, some reactions can show irregular behavior in this regard. One particularly peculiar (but interesting!) phenomenon is that of **oscillating reactions**, in which reactant concentrations can rise and fall as the reaction progresses. One way this can happen is when the products of the reaction (or one of the steps) catalyzes the reaction (or one of the steps). This process is called **autocatalysis**.

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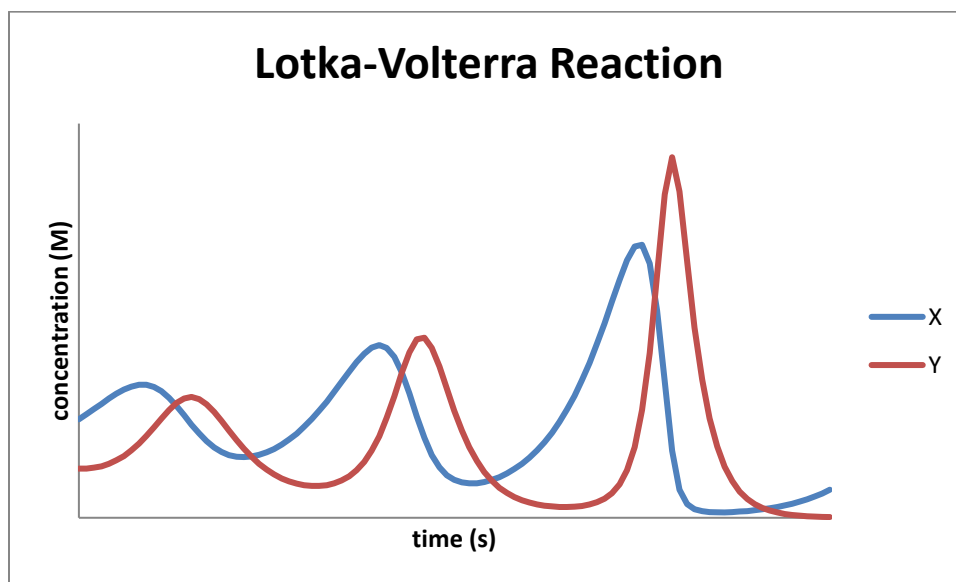
Autocatalysis

An example of an autocatalyzed mechanism is the **Lotka-Volterra mechanism**. This is a three-step mechanism defined as follows:



In this reaction, the concentration of reactant A is held constant by continually adding it to the reaction mixture. The first step is autocatalyzed, so as it proceeds, it speeds up. However, an increase in the production of X by the first reaction increases the rate of the second reaction as well, which is also autocatalyzed. Finally, the removal of Y through the third reaction brings things to a halt, until the first reaction can again produce a buildup of X to start the cycle over.

A plot of the concentration of X and Y as a function of time looks as follows:



This mechanism follows kinetics predicted by what is called the **predator-prey** relationship. In this case, X represents the “prey” and Y represents the “predator”. The population of the predator cannot build up unless there is a significant population of prey on which the predators can feed. Likewise, the population of predators decreases when the population of the prey falls. And finally, there is a lag, as the rise and decline of the prey population controls the rise and fall of the predator population. The equations have been studied extensively and have applications not

just in chemical kinetics, but in biology, economics, and elsewhere. One wonders if the equations can be applied to help to understand politics!

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