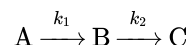


15.2: Complex Rate Laws

It is essential to specify that the order of a reaction and its molecularity are equal only for elementary reactions. Reactions that follow complex laws are composed of several elementary steps, and they usually have non-integer reaction orders, for at least one of the reactants.

Consecutive reactions

A reaction that happens following a sequence of two elementary steps can be written as follows:



Assuming that each of the steps follows a first order kinetic law, and that only the reagent A is present at the beginning of the reaction, we can write the differential change in concentration of each species with respect to infinitesimal time dt , using the following formulas:

$$\begin{aligned} -\frac{d[A]}{dt} &= k_1[A] \Rightarrow [A] = [A]_0 \exp(-k_1 t) \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B]. \end{aligned} \quad (15.2.1)$$

These three equations represent a system of differential equations with three unknown variables. Unfortunately, these equations are linearly dependent on each other, and they are not sufficient to solve the system for each variable. To do so, we need to include a fourth equation, coming from the conservation of mass:

$$[A]_0 = [A] + [B] + [C]. \quad (15.2.2)$$

Using the first equation in Equation 15.2.1, we can now replace the concentration $[A]$ in the second equation and solve for $[B]$:

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 \exp(-k_1 t), \quad (15.2.3)$$

which can be simplified by multiplying both sides by $\exp(k_2 t)$:

$$\begin{aligned} \left(\frac{d[B]}{dt} + k_2[B] \right) \exp(k_2 t) &= k_1[A]_0 \exp[(k_2 - k_1)t] \\ \Rightarrow \frac{d\{[B] \exp(k_2 t)\}}{dt} &= k_1[A]_0 \exp[(k_2 - k_1)t], \end{aligned} \quad (15.2.4)$$

which can then be integrated remembering that $[B]_0 = 0$, and $\int \exp(kx) = \frac{1}{k} \exp(kx)$:

$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 [\exp(-k_1 t) - \exp(-k_2 t)]. \quad (15.2.5)$$

We can then use both $[A]$, from Equation 15.2.1, and $[B]$, from Equation 15.2.5 in Equation 15.2.2 to solve for $[C]$:

$$\begin{aligned} [C] &= [A]_0 - [A] - [B] \\ &= [A]_0 - [A]_0 \exp(-k_1 t) - \frac{k_1}{k_2 - k_1} [A]_0 [\exp(-k_1 t) - \exp(-k_2 t)] \\ &= [A]_0 \left\{ 1 + \frac{-k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t)}{k_2 - k_1} \right\}. \end{aligned} \quad (15.2.6)$$

From these results, we can distinguish two extreme behaviors. The first one is observed when $k_1 \cong k_2$, and it produces a plot of the concentration of species with respect to time reported in Figure 15.2.1. This behavior is observed when a process undergoing a series of consecutive reactions present a rate-determining step in the middle of the sequence (the second reaction, in the simple case analyzed above). Once the process is established, its rate will equate the rate of the slowest step.

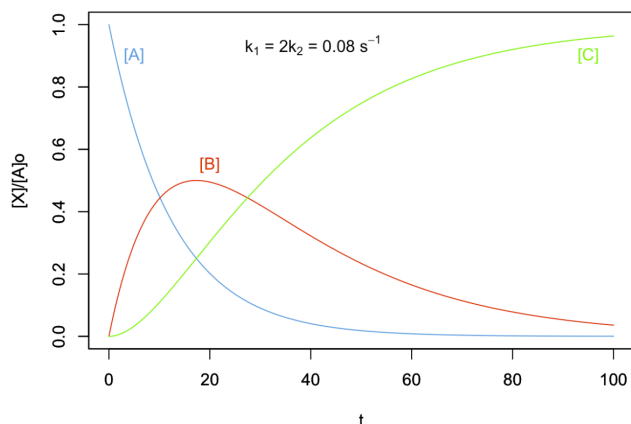


Figure 15.2.1: Concentration Plot for a Process with Two Consecutive Reactions with the Second One Being the Rate-Determining Step.

The second behavior is observed when $k_1 \ll k_2$, and it produces the plot in Figure 15.2.2. In this case, the concentration of the intermediate species B is not relevant throughout the process, and the rate-determining step is the first reaction. As such, the process has the same rate law as an elementary reaction going directly from A to C .

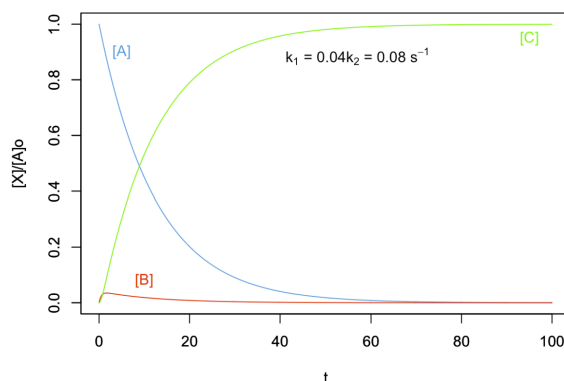
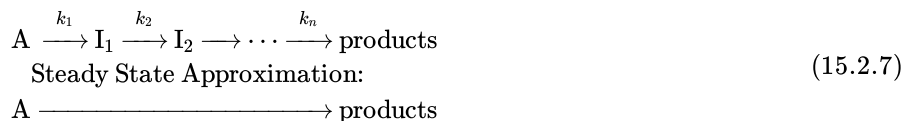


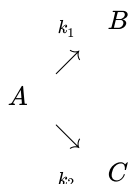
Figure 15.2.2: Concentration Plot for a Process with Two Consecutive Reactions with the First One Being the Rate-Determining Step.

Since the concentration of B is small and relatively constant throughout the process, $\frac{d[B]}{dt} = 0$. We can then simplify the mathematical treatment of these reactions by eliminating it from the process altogether. This simplification is known as the *steady-state approximation*. It is used in chemical kinetics to study processes that undergo a series of reactions producing intermediate species whose concentrations are constants throughout the entire process.



Competitive reactions

A process where two elementary reactions happen in parallel, competing with each can be written as follows:



Assuming that each step follows first order kinetic, we can write:

$$\begin{aligned}
 -\frac{d[A]}{dt} &= k_1[A] + k_2[A] \Rightarrow [A] = [A]_0 \exp[-(k_1 + k_2)t] \\
 \frac{d[B]}{dt} &= k_1[A] \Rightarrow [B] = \frac{k_1}{k_1 + k_2} [A]_0 \{1 - \exp[-(k_1 + k_2)t]\} \\
 \frac{d[C]}{dt} &= k_2[A] \Rightarrow [C] = \frac{k_2}{k_1 + k_2} [A]_0 \{1 - \exp[-(k_1 + k_2)t]\}.
 \end{aligned}$$

The concentration of each of the species can then be plotted against time, obtaining the diagram reported in Figure 15.2.3. The final concentrations of the products, $[B]_f$ and $[C]_f$, will depend on the values of the two rate coefficients. For example, if $k_1 > k_2$, $[B]_f > [C]_f$, as in Figure 15.2.3 but if $k_1 < k_2$, $[B]_f < [C]_f$.

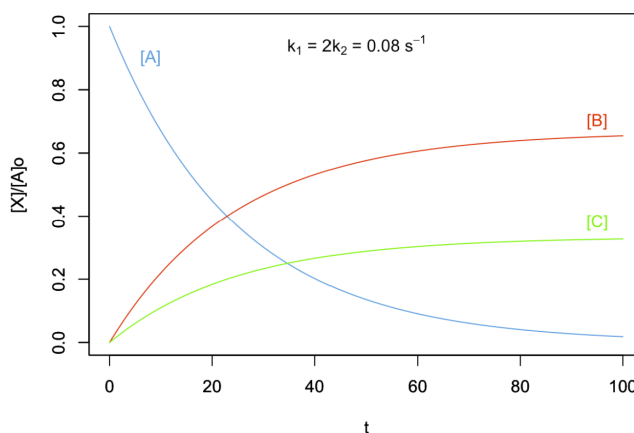


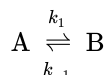
Figure 15.2.3: Concentration Plot for a Process with Two Competitive Reactions.

An important relationship that can be derived from Equation 15.2.1 is that:

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}.$$

Opposed reactions

Another case of complex kinetic law happens when a pair of forward and reverse reactions occur simultaneously:



where the rate coefficients for the forward and backwards reaction, k_1 and k_{-1} respectively, are not necessarily equal to each other, but comparable in magnitude. We can write the rate laws for each of these elementary steps as:

$$\begin{aligned}
 -\frac{d[A]}{dt} &= k_1[A] - k_{-1}[B] = k_1[A] - k_{-1}([A]_0 - [A]) \\
 \frac{d[A]}{dt} &= -(k_1 + k_{-1})[A] + k_{-1}[A]_0,
 \end{aligned} \tag{15.2.8}$$

which can then be integrated to:

$$\begin{aligned}
 [A] &= [A]_0 \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \\
 [B] &= [A]_0 \left\{ 1 - \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \right\}.
 \end{aligned} \tag{15.2.9}$$

These formulas can then be used to obtain the plots in Figure 15.2.4

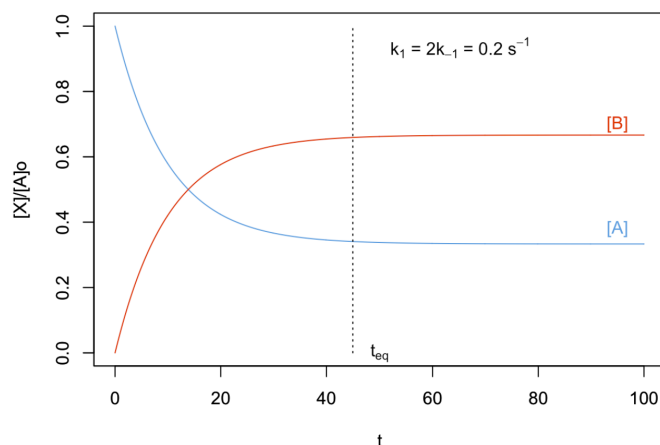


Figure 15.2.4: Concentration Plot for a Process with Two Opposed Reactions.

As can be seen from the plots in Figure 15.2.4 after a sufficiently long time, the systems reach a dynamic equilibrium, where the concentration of A and B don't change. These equilibrium concentrations can be calculated replacing $t = \infty$ in Equation 15.2.8

$$\begin{aligned} [A]_{\text{eq}} &= [A]_0 \frac{k_{-1}}{k_1 + k_{-1}} \\ [B]_{\text{eq}} &= [A]_0 \frac{k_1}{k_1 + k_{-1}}. \end{aligned} \quad (15.2.10)$$

Considering that the concentrations of the species don't change at equilibrium:

$$\begin{aligned} -\frac{d[A]_{\text{eq}}}{dt} &= \frac{d[B]_{\text{eq}}}{dt} = 0 \\ \Rightarrow k_1 [A]_{\text{eq}} &= k_{-1} [B]_{\text{eq}} \\ \Rightarrow \frac{k_1}{k_{-1}} &= \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = K_C, \end{aligned} \quad (15.2.11)$$

where K_C is the equilibrium constant as defined in chapter 10. This is a rare link between kinetics and thermodynamics and appears only for opposed reactions after sufficient time has passed so that the system can reach the dynamic equilibrium.

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