

4.3: Chemical Kinetics

The term chemical kinetics refers to the study of the rates of chemical reactions. As we will see, differential equations play a central role in the mathematical treatment of chemical kinetics. We will start with the simplest examples, and then we will move to more complex cases. As you will see, in this section we will focus on a couple of reaction mechanisms. The common theme will be to find expressions that will allow us to calculate the concentration of the different species that take part of the reaction at different reaction times.

Let's start with the simplest case, in which a reactant A reacts to give the product B. We'll assume the reaction proceeds in one step, meaning there are no intermediates that can be detected.

[Math Processing Error]

We'll use the following notation for the time-dependent concentrations of A and B: $[A]$, $[B]$, or simply $[A]$ and $[B]$. We'll use $[A]$ and $[B]$ to denote the concentrations of A and B at time t . The constant k is the rate constant of the reaction, and is a measure of how fast or slow the reaction is. It depends on the reaction itself (the chemical compounds A and B) and environmental factors such as temperature. The rate constant does not depend on the concentrations of the species involved in the reaction. The units of k depend on the particular mechanism of the reaction, as we will see through the examples. For the case described above, the units will be $1/\text{time}$ (e.g. s^{-1}).

The rate of the reaction (r) will be defined as the number of moles of A that disappear or the number of moles of B that appear per unit of time (e.g. per second) and volume (e.g. liter). This is true because of the stoichiometry of the reaction, as we will discuss in a moment. However, because the rate is a positive quantity, we will use a negative sign if we look at the disappearance of A:

[Math Processing Error]

The rate of the reaction, therefore, is a positive quantity with units of $\text{M}\cdot\text{s}^{-1}$, or in general, concentration per unit of time. As we will see, the rate of the reaction depends on the actual concentration of reactant, and therefore will in general decrease as the reaction progresses and the reactant is converted into product. Although all the molecules of A are identical, they do not need to react at the same instant. Consider the simple mechanism of Equation $\text{A} \rightarrow \text{B}$, and imagine that every molecule of A has a probability p of reacting in every one-second interval. Suppose you start with 1 mole of A in a 1 L flask, and you measure the concentration of A one second later. How many moles of A do you expect to see? To answer this question, you can imagine that you get everybody in China (about one billion people) to throw a die at the same time, and that everybody who gets a six wins the game. How many winners do you expect to see? You know that the probability that each individual gets a six is $1/6$, and therefore one-sixth of the players will win in one round of the game. Therefore, you can predict that the number of winners will be $1/6$ of the total, and the number of losers will be $5/6$. If we get the losers to play a second round, we expect that one-sixth of them will get a six, which accounts for $1/6$ of the total. After the second run, therefore, we'll still have $5/6$ of the total.

Following the same logic, the probability that a molecule of A reacts to give B in each one-second interval is p , and therefore in the first second you expect that p molecules react and $1-p$ remain unreacted. In other words, during the first second of your reaction 0.001 moles of A were converted into B, and therefore the rate of the reaction was p . During the second one-second interval of the reaction you expect that one-thousandth of the remaining molecules will react, and so on. Imagine that you come back one hour later (3,600 s). We expect that p molecules will remain unreacted, which is about p molecules. If you measure the reaction rate in the next second, you expect that one-thousandth of them (p molecules, or p moles) will react to give B. The rate of the reaction, therefore, decreased from p at $t=0$ to p at $t=3600$. You should notice that the fraction of molecules of A that react in each one-second is always the same (in this case one-thousandth). Therefore, the number of molecules that react per time interval is proportional to the number of molecules of A that remain unreacted at any given time. We just concluded that the rate of the reaction is proportional to the concentration of A:

[Math Processing Error]

The proportionality constant, k , is related to the probability that a molecule will react in a small time interval, as we discussed above. In this class, we will concentrate on solving differential equations such as the one above. This is a

very simple differential equation that can be solved using different initial conditions. Let's say that our goal is to find both $[A]$ and $[B]$. As chemists, we need to keep in mind that the law of mass conservation requires that

[Math Processing Error]

In plain English, the concentrations of A and B at any time need to add up to the sum of the initial concentrations, as one molecule of A converts into B, and we cannot create or destroy matter. Again, keep in mind that this equation will need to be modified according to the stoichiometry of the reaction. We will call an equation of this type a 'mass balance'.

Before solving this equation, let's look at other examples. What are the differential equations that describe this sequential mechanism?

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In this mechanism, A is converted into C through an intermediate, B. Everything we discussed so far will apply to each of these two elementary reactions (the two that make up the overall mechanism). From the point of view of A nothing changes. Because the rate of the first reaction does not depend on B, it is irrelevant that B is converted into C (imagine you give 1 dollar per day to a friend. It does not matter whether your friend saves the money or gives it to someone else, you still lose 1 dollar per day).

[Math Processing Error]

On the other hand, the rate of change of $[B]$, *[Math Processing Error]* is the sum of the rate at which B is created (*[Math Processing Error]*), minus the rate at which it disappears by reacting into C (*[Math Processing Error]*):

[Math Processing Error]

This can be read: The rate of change of $[B]$ equals the rate at which $[B]$ appears from A into B, minus the rate at which $[B]$ disappears from B into C. In each term, the rate is proportional to the reactant of the corresponding step: A for the first reaction, and B for the second step.

What about C? Again, it is irrelevant that B was created from A (if you get 1 dollar a day from your friend, you don't care if she got it from her parents, you still get 1 dollar per day). The rate at which C appears is proportional to the reactant in the second step: B. Therefore:

[Math Processing Error]

The last three equations form a system of differential equations that need to be solved considering the initial conditions of the problem (e.g. initially we have A but not B or C). We'll solve this problem in a moment, but we still need to discuss a few issues related to how we write the differential equations that describe a particular mechanism. Imagine that we are interested in

[Math Processing Error]

We know that the rate of a reaction is defined as the change in concentration with time...but which concentration? is it *[Math Processing Error]*? or *[Math Processing Error]*? or *[Math Processing Error]*? These are all different because 3 molecules of C are created each time 1 of B and 2 of A disappear. Which one should we use? Because 2 of A disappear every time 1 of B disappears: *[Math Processing Error]*. Now, considering that rates are positive quantities, and that the derivatives for the reactants, *[Math Processing Error]* and *[Math Processing Error]*, are negative:

[Math Processing Error]

This example shows how to deal with the stoichiometric coefficients of the reaction. Note that in all our examples we assume that the reactions proceed as written, without any 'hidden' intermediate steps.

First order reactions

We have covered enough background, so we can start solving the mechanisms we introduced. Let's start with the easiest one (Equations *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*):

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

This mechanism is called a first order reaction because the rate is proportional to the first power of the concentration of reactant. For a second-order reaction, the rate is proportional to the square of the concentration of reactant (see Problem [\[Math Processing Error\]](#)). Let's start by finding [\[Math Processing Error\]](#) from [\[Math Processing Error\]](#). We'll then obtain [\[Math Processing Error\]](#) from the mass balance. This is a very simple differential equation because it is separable:

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

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

We integrate both sides of the equation, and combine the two integration constants in one:

$$\ln[A] = -kt + C$$

We need to solve for $[A]$:

$$[A] = e^{-kt + C}$$

This is the general solution of the problem. Let's assume we are giving the following initial conditions: $[A]$ [\[Math Processing Error\]](#), $[B]$ [\[Math Processing Error\]](#) We'll use this information to find the arbitrary constant [\[Math Processing Error\]](#):

$$[A] = [A]_0 e^{-kt}$$

Therefore, the particular solution is:

$$[A] = [A]_0 e^{-kt}$$

What about $[B]$? From the mass balance, $[B] = [A]$ [\[Math Processing Error\]](#) + $[B]$ [\[Math Processing Error\]](#) - $[A] = [A]$ [\[Math Processing Error\]](#) - $[A]$ [\[Math Processing Error\]](#).

Figure [\[Math Processing Error\]](#) shows three examples of decays with different rate constants.

We can calculate the half-life of the reaction ([\[Math Processing Error\]](#)), defined as the time required for half the initial concentration of A to react. From Equation [\[Math Processing Error\]](#):

$$[A] = [A]_0 e^{-kt}$$

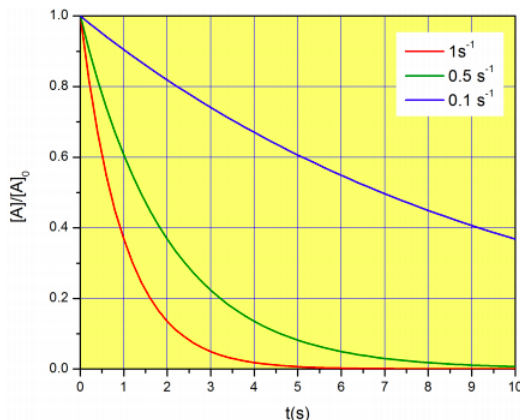


Figure [\[Math Processing Error\]](#): Time-dependent concentration of the reactant in the reaction [\[Math Processing Error\]](#) (CC BY-NC-SA; [Marcia Levitus](#))

When [\[Math Processing Error\]](#),

$$[A] = [A]_0 e^{-kt}$$

$$[A] = [A]_0 e^{-kt}$$

$$[A] = [A]_0 e^{-kt}$$

Note that in this case, the half-life does not depend on the initial concentration of A. This will not be the case for other types of mechanisms. Also, notice that we have already covered the concept of half-life in [Chapter 1](#) (see Figure [\[Math Processing Error\]](#)), so this might be a good time to read that section again and refresh what we have already learned about sketching exponential decays.

In physical chemistry, scientists often talk about the ‘relaxation time’ instead of the half-life. The relaxation time $t = \tau$ for a decay of the shape $[A]/[A]_0 = e^{-t/\tau}$ is $t = \tau$, so in this case, the relaxation time is simply $t = \tau$. Notice that the relaxation time has units of time, and it represents the time at which the concentration has decayed to $[A]/[A]_0 \approx 0.37$ of its original value:

$$[A]/[A]_0 = e^{-t/\tau} \quad t = \tau$$

The half-life and relaxation time are compared in Figure 1 for a reaction with $k = 0.347 \text{ s}^{-1}$.

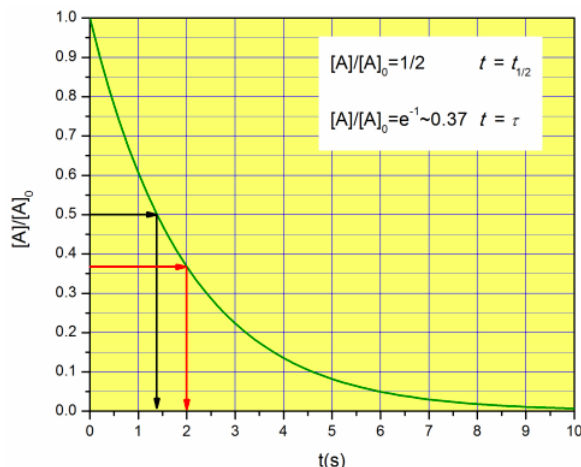


Figure 1: Half-life (black) and relaxation time (red) for the reaction $A \rightarrow B$ with $k = 0.347 \text{ s}^{-1}$ (CC BY-NC-SA; Marcia Levitus)

Consecutive First Order Processes

We will now analyze a more complex mechanism, which involves the formation of an intermediate species (B):



which is mathematically described by Equations (1), (2) and (3). Let's assume that initially the concentration of A is $[A]_0$, and the concentrations of B and C are zero. In addition, we can write a mass balance, which for these initial conditions is expressed as:

$$[A] + [B] + [C] = [A]_0$$

Let's summarize the equations we have:

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned}$$

Note that Equation (1) is not independent from Equations (2)-(3). If you take the derivative of (2) you get (3), which is the same you get if you add Equations (2)-(3). This means that Equations (1)-(3) are not all independent, and three of them are enough for us to solve the problem. As you will see, the mass balance (4) will give us a very easy way of solving for [C] once we have [A] and [B], so we will use it instead of Equation (3).

We need to solve the system of Equations (1)-(2), and although there are methods to solve systems of differential equations (e.g. using linear algebra), this one is easy enough that can be solved with what we learned so far. This is because not all equations contain all variables. In particular, Equation (1) is a simple separable equation with dependent variable [A], which can be solved independently of [B] and [C]. We in fact just solved this equation in the First Order Reactions section, so let's write down the result:

$$[A] = [A]_0 e^{-k_1 t}$$

Equation (2) contains two dependent variables, but luckily we just obtained an expression for one of them. We can now re-write (2) as:

[Math Processing Error]

Equation [Math Processing Error] contains only one dependent variable, $[B]$, one independent variable, [Math Processing Error], and three constants: [Math Processing Error], [Math Processing Error] and [Math Processing Error]. This is therefore an ordinary differential equation, and if it is either separable or linear, we will be able to solve it with the techniques we learned in this chapter. Recall eq. [sep], and verify that Equation [Math Processing Error] cannot be separated as

[Math Processing Error]

Equation [Math Processing Error] is not separable. Is it linear? Recall Equation [Math Processing Error] and check if you can write this equation as [Math Processing Error]. We in fact can:

[Math Processing Error]

Let's use the list of steps delineated in Section 4.2. We need to calculate the integrating factor, [Math Processing Error], which in this case is [Math Processing Error]. We then multiply Equation [Math Processing Error] by the integrating factor:

[Math Processing Error]

In the next step, we need to recognize that the left-hand side of the equation is the derivative of the product of the dependent variable times the integrating factor:

[Math Processing Error]

We then take '[Math Processing Error]' to the right side of the equation and integrate both sides:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

We have an arbitrary constant because this is a first order differential equation. Let's calculate [Math Processing Error] using the initial condition [Math Processing Error]:

[Math Processing Error]

[Math Processing Error]

And therefore,

[Math Processing Error]

[Math Processing Error]

Before moving on, notice that we have assumed that [Math Processing Error]. We were not explicit, but we performed the integration with this assumption. If [Math Processing Error] the exponential term becomes 1, which is not a function of [Math Processing Error]. In this case, the integral will obviously be different, so our answer assumes [Math Processing Error]. This is good news, since otherwise we would need to worry about the denominator of [eq:b(t)] being zero. You will solve the case [Math Processing Error] in Problem 4.4.

Now that we have $[A]$ and $[B]$, we can get the expression for $[C]$. We could use Equation [Math Processing Error]:

[Math Processing Error]

This is not too difficult because the equation is separable. However, it is easier to get $[C]$ from the mass balance, Equation [Math Processing Error]:

[Math Processing Error]

Plugging the answers we got for $[A]$ and $[B]$:

[Math Processing Error]

[Math Processing Error]

Equations [Math Processing Error], [Math Processing Error], [Math Processing Error] are the solutions we were looking for. If we had the values of [Math Processing Error] and [Math Processing Error] we could plot [Math Processing Error], [Math

Processing Error and *[Math Processing Error]* and see how the three species evolve with time. If we had *[Math Processing Error]* we could plot the actual concentrations, but notice that this does not add too much, because it just re-scales the *[Math Processing Error]* axis but does not change the shape of the curves.

Figure *[Math Processing Error]* shows the concentration profiles for a reaction with *[Math Processing Error]* and *[Math Processing Error]*. Notice that because B is an intermediate, its concentration first increases, but then decreases as B is converted into C. The product C has a 'lag phase', because we need to wait until enough B is formed before we can see the concentration of C increase (first couple of seconds in this example). As you will see after solving your homework problems, the time at which the intermediate (B) achieves its maximum concentration depends on both *[Math Processing Error]* and *[Math Processing Error]*.

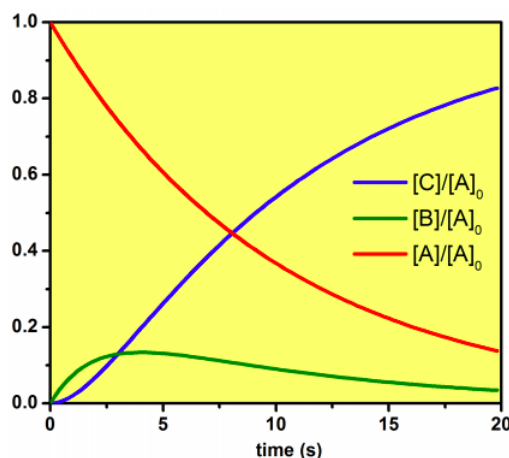


Figure *[Math Processing Error]*: Concentration profiles for the reaction *[Math Processing Error]* with *[Math Processing Error]* and *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

Reversible first order reactions

So far we have discussed irreversible reactions. Yet, we know that many reactions are reversible, meaning that the reactant and product exist in equilibrium:



The rate of change of [A], *[Math Processing Error]*, is the rate at which A appears (*[Math Processing Error]*) minus the rate at which A disappears (*[Math Processing Error]*):

$$[Math Processing Error]$$

We cannot solve this equation as it is, because it has two dependent variables, [A] and [B]. However, we can write [B] in terms of [A], or [A] in terms of [B], by using the mass balance:

$$[Math Processing Error]$$

$$[Math Processing Error]$$

$$[Math Processing Error]$$

This is an ordinary, separable, first order differential equation, so it can be solved by direct integration. You will solve this problem in your homework, so let's skip the steps and jump to the answer:

$$[Math Processing Error]$$

This is a reversible reaction, so if we wait long enough it will reach equilibrium. The concentration of [A] in equilibrium, *[A][Math Processing Error]*, is the limit of the previous expression when *[Math Processing Error]*. Because *[Math Processing Error]* when *[Math Processing Error]*:

$$[Math Processing Error]$$

and we can re-write Equation *[Math Processing Error]* as

$$[Math Processing Error]$$

As you will do in your homework, we can calculate *[Math Processing Error]* from the mass balance as *[Math Processing Error]*.

Equation [Math Processing Error] is not too different from Equation [Math Processing Error]. In the case of an irreversible reaction, (Equation [Math Processing Error]), $[A]$ decays from an initial value $[A]_0$ to a final value [Math Processing Error] with a relaxation time [Math Processing Error]. For the reversible reaction, [Math Processing Error] decays from an initial value [Math Processing Error] to a final value [Math Processing Error] with a relaxation time [Math Processing Error]. This last statement is not trivial! It says that the rate at which a reaction approaches equilibrium depends on the sum of the forward and backward rate constants.

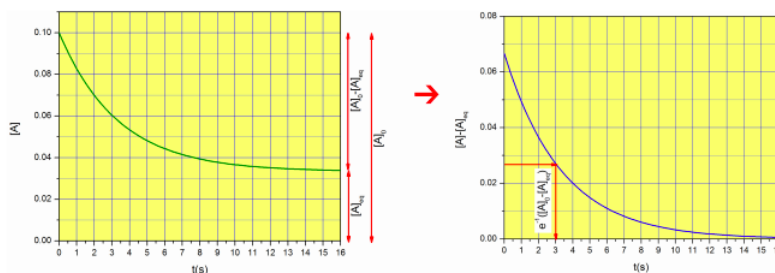


Figure [Math Processing Error]: The kinetics of a reaction with [Math Processing Error], [Math Processing Error] and [Math Processing Error] approaching equilibrium. Note that the relaxation time is [Math Processing Error] (CC BY-NC-SA; Marcia Levitus)

In your homework you will be asked to prove that the ratio of the concentrations in equilibrium, [Math Processing Error] is equal to the ratio of the forward and backwards rate constants. In addition, from your introductory chemistry courses you should know that the equilibrium constant of a reaction ([Math Processing Error]) is the ratio of the equilibrium concentrations of product of reactant. Therefore:

$$[Math Processing Error]$$

This means that we can calculate the ratio of [Math Processing Error] and [Math Processing Error] from the concentrations of A and B we observe once equilibrium has been reached (i.e. once [Math Processing Error]). At the same time, we can obtain the sum of [Math Processing Error] and [Math Processing Error] from the relaxation time of the process. If we have the sum and the ratio, we can calculate both [Math Processing Error] and [Math Processing Error]. This all makes sense, but it requires that we can watch the reaction from an initial state outside equilibrium. If the system is already in equilibrium, [Math Processing Error], and [Math Processing Error] at all times. A plot of $[A]$ [Math Processing Error] will look flat, and we will not be able to extract the relaxation time of the reaction. If, however, we have an experimental way of shifting the equilibrium so [Math Processing Error], we can measure the relaxation time by observing how the reaction returns to its equilibrium position.

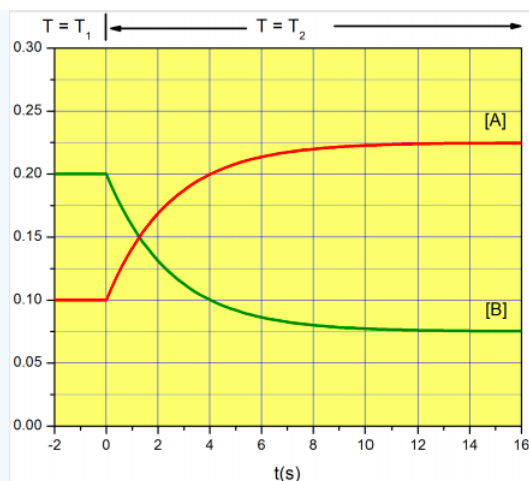
Advanced topic: How can we shift the equilibrium? One way is to produce a very quick change in the temperature of the system. The equilibrium constant of a reaction usually depends on temperature, so if a system is equilibrated at a given temperature (say [Math Processing Error]), and we suddenly increase the temperature (e.g. to [Math Processing Error]), the reaction will suddenly be away from its equilibrium condition at the new temperature. We can watch the system relax to the equilibrium concentrations at [Math Processing Error], and measure the relaxation time. This will allow us to calculate the rate constants at [Math Processing Error].

$$[Math Processing Error]$$

✓ Example [Math Processing Error]

Advanced topic The following figure illustrates the experimental procedure known as “T-jump”, in which a sudden change in temperature is used to shift the position of a reversible reaction out of equilibrium. The experiment starts at a temperature [Math Processing Error], and the temperature is increased to [Math Processing Error] instantaneously at time [Math Processing Error]. Because the equilibrium constant at [Math Processing Error] is different from the equilibrium constant at [Math Processing Error], the system needs to relax to the new equilibrium state. From the graph below estimate to the best of your abilities [Math Processing Error], [Math Processing Error], and the rate constants [Math Processing Error], and [Math Processing Error] at [Math Processing Error].

$$[Math Processing Error]$$



Solution

At $t = 0$, $[A] = 0.10$ and $[B] = 0.20$. The equilibrium constant is $K = 2.0$.

At $t = \infty$, $[A] = 0.22$ and $[B] = 0.08$. The equilibrium constant is $K = 2.0$.

Because $K = 2.0$, at $t = 0$, $[A] = 0.10$ and $[B] = 0.20$. To calculate the relaxation time let's look at the expression for K (Equation 4.3.8).

$$K = \frac{[A]}{[B]}$$

When the time equals the relaxation time ($t = \tau$),

$$K = \frac{[A]}{[B]}$$

$$[A] = 2[B]$$

From the graph, $[A] = 0.15$ at $t = 1.5$, and therefore the relaxation time is $\tau = 1.5$ s.

We have $[A] = 0.15$ and $[B] = 0.15$:

$$K = \frac{[A]}{[B]}$$