

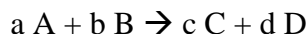
Chapter 11: Chemical Kinetics I – Reaction Rates

Chemical kinetics is the study of how fast chemical reactions proceed from reactants to products. This is an important topic because while thermodynamics will tell us about the direction of spontaneous change, it is silent as to how fast processes will occur. But additionally, the power of studying reaction rates is that it gives us insight into the actual pathways chemical processes follow to proceed from reactants to products.

Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction



the reaction rate can be defined by any of the ratios

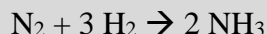
$$rate = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Or for infinitesimal time intervals

$$rate = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Example:

Under a certain set of conditions, the rate of the reaction



the reaction rate is 6.0×10^{-4} M/s. Calculate the time-rate of change for the concentrations of N_2 , H_2 , and NH_3 .

Solution:

Due to the stoichiometry of the reaction,

$$rate = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

So

$$\frac{d[N_2]}{dt} = -6.0 \cdot 10^{-4} \frac{M}{s}$$

$$\frac{d[H_2]}{dt} = -18.0 \cdot 10^{-4} \frac{M}{s}$$

$$\frac{d[NH_3]}{dt} = 12.0 \cdot 10^{-4} \frac{M}{s}$$

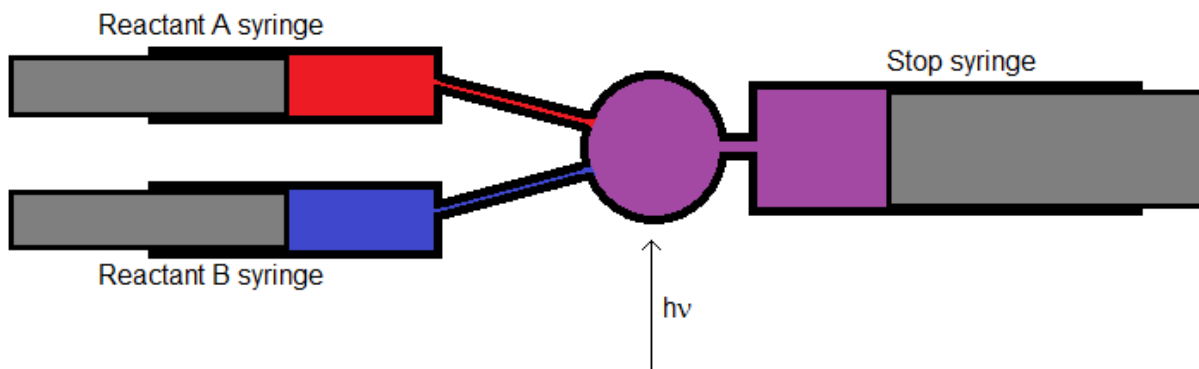
Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

Measuring Reaction Rates

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

The Stopped-Flow Method

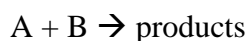
The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

Rate Laws

A rate law is any mathematical relationship that relates the concentration of a reactant or product in a chemical reaction to time. Rate laws can be expressed in either derivative (or ratio, for finite time intervals) or integrated form. One of the more common general forms a rate law for the reaction



may take is

$$\text{rate} = k[A]^\alpha[B]^\beta$$

where k , α , and β are experimentally determined values. However, a rate law can take many different forms, some of which can be quite intricate and complex. The powers α and β need not be integers. For example

$$\text{rate} = k[A][B]^{\frac{1}{2}}$$

is a rate law that is observed for some reactions. Sometimes, the concentrations of products must be included.

$$\text{rate} = k \frac{[A]^{\frac{1}{2}}[B]}{[P]}$$

In some cases, the concentration of a catalyst or enzyme is important. For example, many enzyme mediated reactions in biological systems follow the Michaelis-Menten rate law, which is of the form

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

where v_{\max} and K_M are factors that are determined experimentally, and $[S]$ is the concentration of the substrate in the reaction.

Order

For those cases where the rate law can be expressed in the form

$$rate = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

where A, B, and C are reactants (or products or catalysts, etc.) involved in the reaction, the reaction is said to be of α order in A, β order in B, and γ order in C. The reaction is said to be $\alpha + \beta + \gamma$ order overall. Some examples are shown in the following table:

Rate law	Order with respect to A	Order with respect to B	Order with respect to C	Overall order
$rate = k$	0	0	0	0
$rate = k[A]$	1	0	0	1
$rate = k[A]^2$	2	0	0	2
$rate = k[A][B]$	1	1	0	2
$rate = k[A]^2[B]$	2	1	0	3
$rate = k[A][B][C]$	1	1	1	3

Reaction orders can also be fractional such as

$$rate = k[A][B]^{\frac{1}{2}}$$

which is 1st order in A, and half order in B. The order can also be negative such as

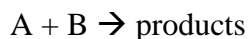
$$rate = k \frac{[A]}{[B]}$$

which is 1st order in A, and -1 order in B. In this case, an build-up of the concentration of B will retard (slow) the reaction.

In all cases, the order of the reaction with respect to a specific reactant or product (or catalyst, or whatever) must be determined experimentally. As a general rule, the stoichiometry cannot be used to predict the form of the rate law. However, the rate law can be used to gain some insight into the possible pathways by which the reaction can proceed. That is the topic of Chapter 12. For now we will focus on three useful methods that are commonly used in chemistry to determine the rate law for a reaction from experimental data.

Empirical Methods

Perhaps the simplest of the methods to be used are the empirical methods, which rely on the qualitative interpretation of a graphical representation of the concentration vs time profile. In these methods, some function of concentration is plotted as a function of time, and the result is examined for a linear relationship. For the following examples, consider a reaction of the form



in which A is one of the reactants. In order to employ these empirical methods, one must generate the forms of the integrated rate laws.

0th order rate law

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

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

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time $t = 0$, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_0}^{[A]} d[A] = -k \int_{t=0}^{t=t} dt$$

which yields

$$[A] - [A]_0 = -kt$$

or

$$[A] = [A]_0 - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is $-k$, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0th order kinetics. If they are not, other possibilities must be considered.

1st order rate law

A first order rate law would take the form

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

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

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

This expression is also easily integrated as before

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_0 = kt$$

or

$$\ln[A] = \ln[A]_0 - kt$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of $\ln[A]$ as a function of time should produce a linear plot, the slope of which is $-k$, and the intercept of which is $\ln[A]_0$.

Example:

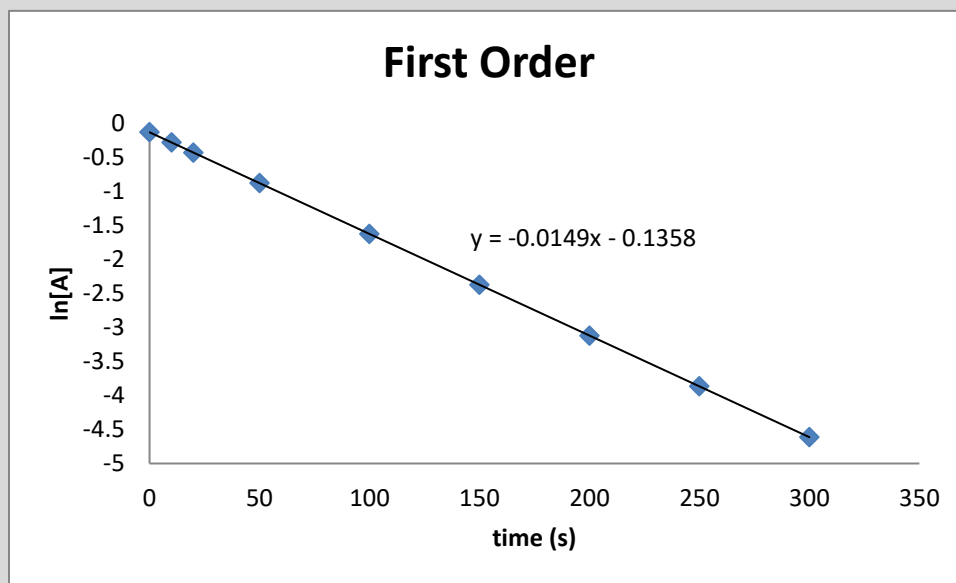
Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

time (s)	[A] (M)
0	0.873
10	0.752
20	0.648
50	0.414
100	0.196

150	0.093
200	0.044
250	0.021
300	0.010

Solution:

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1} . The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law can be expressed in exponential form:

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

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

Example:

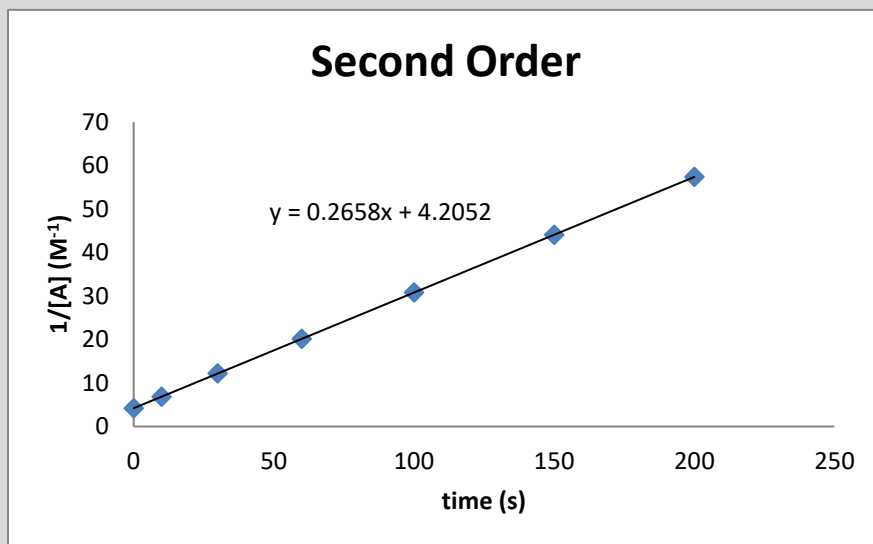
Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

time (s)	[A] (M)
0	0.238
10	0.161

30	0.098
60	0.062
100	0.041
150	0.029
200	0.023

Solution:

The plot looks as follows:



From this plot, it can be seen that the rate constant is $0.2658 \text{ M}^{-1} \text{ s}^{-1}$. The concentration at time $t = 0$ can also be inferred from the intercept.

2nd order rate laws

If the reaction follows a second order rate law, the same methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k dt$$

The integration then becomes

Thermochemistry and Chemical Kinetics: Chemical Kinetics I © 2021 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_{t=0}^{t=t} dt$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result is of integration is

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k , and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type



That has a rate law given by

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

the integration will depend on the decrease of $[A]$ and $[B]$ (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product $[P]$.

$$[A] = [A]_{t=0} - [P] \quad \text{and} \quad [B] = [B]_{t=0} - [P]$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

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

Substituting the relationships for [A] and [B] into the rate law yields

$$\frac{d[P]}{dt} = k([A]_0 - [P])([B]_0 - [P])$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_0 - [P])([B]_0 - [P])} = k dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_0^{[P]} \frac{d[P]}{([A]_0 - [P])([B]_0 - [P])} = k \int_0^t dt$$

Consulting a table of integrals reveals that for $a \neq b$ ¹,

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a} \ln \left(\frac{b-x}{a-x} \right)$$

Applying the definite integral (for $[A]_0 \neq [B]_0$) results in

$$\left[\frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]_0 - [P]}{[A]_0 - [P]} \right) \right]_0^{[P]} = k[t]_0^t$$

$$\frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]_0 - [P]}{[A]_0 - [P]} \right) - \frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]_0}{[A]_0} \right) = kt$$

Recalling that

$$[A] = [A]_0 - [P] \quad \text{and} \quad [B] = [B]_0 - [P]$$

Substituting into the integrated rate law and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B][A]_0}{[A][B]_0} \right) = kt$$

¹ This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is $([B]_0 - [A]_0)k$.

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

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

And the integrated rate law is (as before)

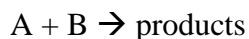
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

The results of the integration of these simple rate laws can be summarized in the following table.

Order	Reaction	Integrated rate law	Linear plot
0		$[A] = [A]_0 - kt$	$[A] \text{ vs. } t$
1		$\ln[A] = \ln[A]_0 - kt$ $[A] = [A]_0 e^{-kt}$	$\ln[A] \text{ vs. } t$
2	$A + A \rightarrow P$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]} \text{ vs. } t$
	$A + B \rightarrow P$	$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B][A]_0}{[A][B]_0}\right) = kt$	$\ln\left(\frac{[B]}{[A]}\right) \text{ vs. } t$

The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction



might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^\alpha[B]^\beta$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^\alpha[B]_i^\beta}{k[A]_j^\alpha[B]_j^\beta}$$

So using runs 1 and 2,

$$\frac{0.0347 \frac{M}{s}}{0.0694 \frac{M}{s}} = \frac{k(0.0100 M)^\alpha(0.0100 M)^\beta}{k(0.0200 M)^\alpha(0.0100 M)^\beta}$$

This simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^\alpha$$

So clearly, $\alpha = 1$ and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694 \frac{M}{s}}{0.2776 \frac{M}{s}} = \frac{k(0.0200 M)(0.0100 M)^\beta}{k(0.0200 M)(0.0200 M)^\beta}$$

This simplifies to

$$\left(\frac{1}{4}\right) = \left(\frac{1}{2}\right)^\beta$$

By inspection, one can conclude that $\beta = 2$, and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of β can be determined by taking the natural logarithm of both sides of the expression.

$$\ln\left(\frac{1}{4}\right) = \beta \ln\left(\frac{1}{2}\right)$$

Dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law can be expressed as

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

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Using the first run,

$$0.0347 \frac{M}{s} = k(0.0100 M)(0.0100 M)^2$$

This results in a value of k

$$k = 3.47 \cdot 10^5 M^{-2}s^{-1}$$

It is useful to note that the units on k are consistent with a 3rd order rate law.

The Method of Half-Lives

Another method for determining the order of a reaction is to examine the behavior of the **half-life** as the reaction progresses. The half-life can be defined as the time it takes for the concentration of a reactant to fall to half of its original value. The method of half-lives involved measuring the half-life's dependence on concentration. The expected behavior can be predicted using the integrated rate laws we derived earlier.

Using the definition of the half-life, at time $t_{1/2}$ the concentration $[A]$ drops to half of its original value, $[A]_0$.

$$[A] = \frac{1}{2} [A]_0 \quad \text{at} \quad t = t_{1/2}$$

So if the reaction is 0th order in A, after one half-life

$$\frac{1}{2} [A]_0 = [A]_0 - k t_{1/2}$$

Solving for $t_{1/2}$ reveals the dependence of the half-life on the initial concentration.

$$\frac{[A]_0}{2k} = t_{1/2}$$

So as the original concentration is decreased, the half-life of a 0th order reaction will also decrease.

Similarly, for a first order reaction,

$$\frac{1}{2} [A]_0 = [A]_0 e^{-k t_{1/2}}$$

And solving for $t_{1/2}$ results in a concentration independent expression

$$\frac{\ln(2)}{k} = t_{1/2}$$

It is because the half-life of a 1st order reaction is independent of concentration that it is oftentimes used to describe the rate of first order processes (such as radioactive decay.)

For a 2nd order reaction, the half-life can be expressed based on the integrated rate law.

$$\frac{1}{\frac{1}{2} [A]_0} = \frac{1}{[A]_0} + k t_{1/2}$$

Solving for $t_{1/2}$ yields

$$\frac{1}{[A]_0 k} = t_{1/2}$$

In the case of a second order reaction, the half-life increases with decreasing initial concentration.

Order	Half-life	Behavior
0 th	$t_{1/2} = \frac{[A]}{2k}$	Decreases as the reaction progresses (as [A] decreases)
1 st	$t_{1/2} = \frac{\ln 2}{k}$	Remains constant as the reaction progresses (is independent of concentration)
2 nd	$t_{1/2} = \frac{1}{k[A]}$	Increases with decreasing concentration.

For reactions in which the rate law depends on the concentration of more than one species, the half-life can take a much more complex form that may depend on the initial concentrations of multiple reactants, or for that matter, products!

Example:

Carbon-14 decays with a half-life of 5730 years. What is the rate constant for the decay process? What percentage of carbon-14 will remain after a biological sample has stopped ingesting carbon-14 for 1482 years?

Solution:

The rate constant is fairly easy to calculate:

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{5730 \text{ yr}} = 1.21 \cdot 10^{-4} \text{ yr}^{-1}$$

Now the integrated rate law can be used to solve the second part of the problem.

$$\% \text{ } ^{14}\text{C} = (100\%)e^{(-1.21 \cdot 10^{-4} \text{ yr}^{-1})(1482 \text{ yr})}$$

$$\% \text{ } ^{14}\text{C} = 83.6 \%$$

Example:

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0th order, 1st order, or 2nd order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480

40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution:

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

[A] ₀ (M)	1.200	0.800	0.600	0.400
t _{1/2} (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A] t_{1/2}}$$

$$k = \frac{1}{(0.800 \text{ M})(30 \text{ s})} = 0.0417 \text{ M}^{-1} \text{ s}^{-1}$$

Temperature Dependence

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-\frac{E_a}{RT}}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

If the rate constant for a reaction is measured at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression of the Arrhenius model:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example:

For a given reaction, the rate constant doubles when the temperature is increased from 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution:

The energy of activation can be calculated from the following.

$$\ln\left(\frac{2k}{k}\right) = -\frac{E_a}{8.314 \frac{J}{mol\ K}}\left(\frac{1}{308\ K} - \frac{1}{298\ K}\right)$$

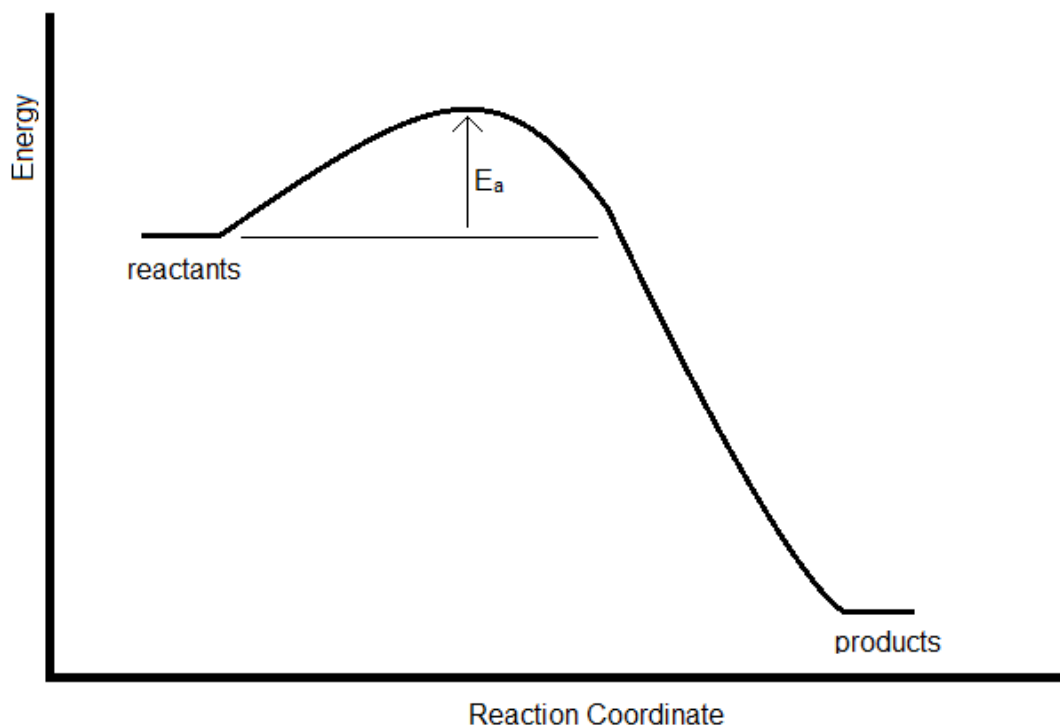
From this, $E_a = 52.9\text{ kJ/mol}$.

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.



Collision Theory

Collision Theory was first introduced in the 1910s by Max Trautz (Trautz, 1916) and William Lewis (Lewis, 1918) to try to account for the magnitudes of rate constants in terms of the frequency of molecular collisions, the collisional energy, and the relative orientations of the molecules involved in the collision.

The rate of a reaction, according to collision theory, can be expressed as

$$rate = Z_{AB}F$$

where Z_{AB} is the frequency of collisions between the molecules A and B involved in the reaction, and F is the fraction of those collisions that will lead to a reaction. The factor F has two important contributors, the energy of the collision and the orientation of the molecules when they collide. The first term, Z_{AB} , can be taken from the kinetic molecular theory discussed in Chapter 2.

$$Z_{AB} = \left(\frac{8k_B T}{\pi \mu} \right)^{\frac{1}{2}} \sigma_{AB} [A][B]$$

Where the first term is the average relative velocity in which μ is the reduced mass of the A-B collisional system, σ_{AB} is the collisional cross section, and $[A]$ and $[B]$ give the concentrations of A and B.

Thermochemistry and Chemical Kinetics: Chemical Kinetics I © 2021 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

The factor F depends on the activation energy. Assuming a Boltzmann (or Boltzmann-like) distribution of energies, the fraction of molecular collisions that will have enough energy to overcome the activation barrier is given by

$$F = e^{-\frac{E_a}{RT}}$$

And so the rate of the reaction is predicted by

$$rate = \left(\frac{8k_B T}{\pi\mu}\right)^{\frac{1}{2}} \sigma_{AB} [A][B] e^{-\frac{E_a}{RT}}$$

So if the rate law can be expressed as a second order rate law

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

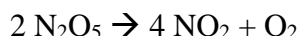
it is clear that the rate constant k is given by

$$k = \left(\frac{8k_B T}{\pi\mu}\right)^{\frac{1}{2}} \sigma_{AB} e^{-\frac{E_a}{RT}}$$

By comparison, the theory predicts the form of the **Arrhenius prefactor** to be

$$A = \left(\frac{8k_B T}{\pi\mu}\right)^{\frac{1}{2}} \sigma_{AB}$$

It should be noted that collision theory appears to apply only to bimolecular reactions, since it takes two molecules to collide. But there are many reactions that have first order rate laws, but are initiated by bimolecular steps in the mechanisms. (Reaction mechanisms will form a large part of the discussion in Chapter 12.) Consider as an example, the decomposition of N_2O_5 , which follows the reaction

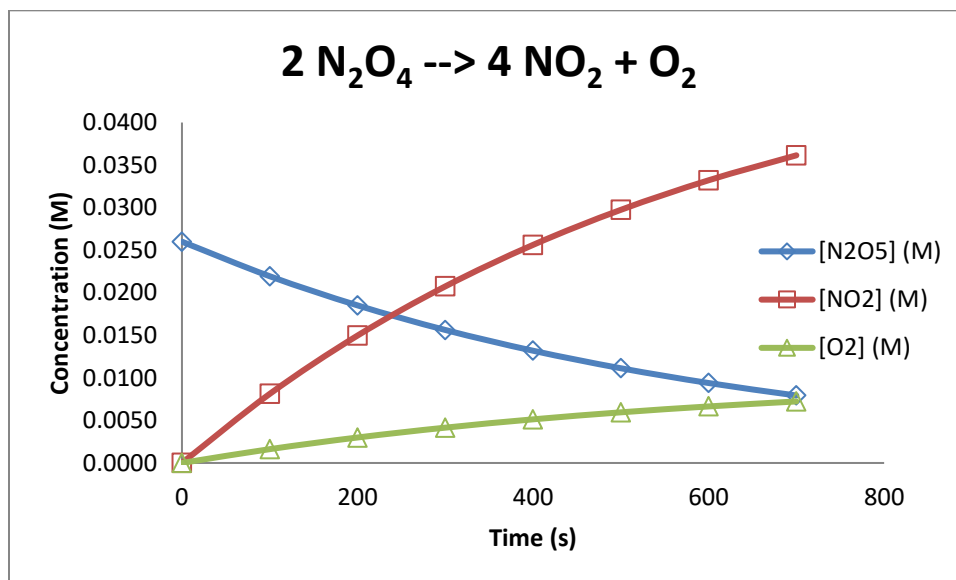


Under a certain set of conditions, the following concentrations are observed as a function of time.

time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
0	0.0260	0.0000	0.0000
100	0.0219	0.0081	0.0016
200	0.0185	0.0150	0.0030
300	0.0156	0.0207	0.0041

400	0.0132	0.0256	0.0051
500	0.0111	0.0297	0.0059
600	0.0094	0.0332	0.0066
700	0.0079	0.0361	0.0072

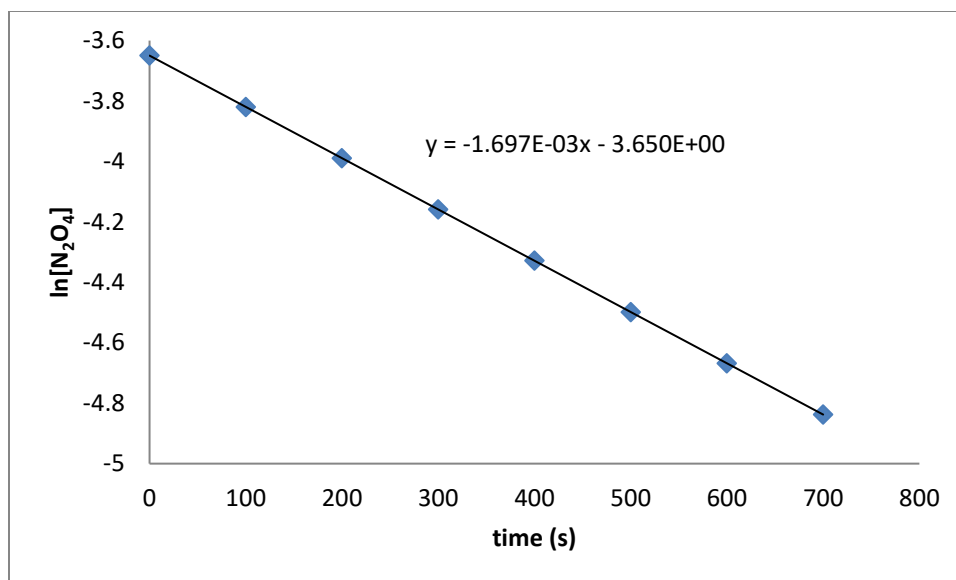
Graphically, these data look as follows:



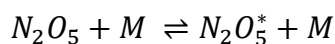
The data for N_2O_5 can be analyzed empirically to show that the reaction is first order in N_2O_5 , with a rate constant of $1.697 \times 10^{-3} \text{ s}^{-1}$. (The graph is shown below.) So the rate law for the reaction is

$$\text{rate} = 1.697 \cdot 10^{-3} \text{ s}^{-1} [\text{N}_2\text{O}_5]$$

So how can collision theory be used to understand the rate constant? As it turns out, the mechanism for the reaction involves a bimolecular initiation step.



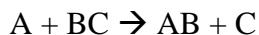
The mechanism for the reaction has a bimolecular initiation step



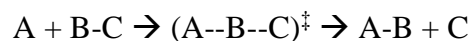
where $N_2O_5^*$ is an energetically activated form of N_2O_5 which can either relax to reform N_2O_5 or decompose to form the products of the reaction. Because the initiation step is bimolecular, collision theory *can* be used to understand the rate law, but because the product of the unimolecular step undergoes slow conversion to products unimolecularly, the overall rate is observed to be first order in N_2O_5 . The analysis of reaction mechanisms, and reconciliation with observed rate laws, form the subjects of Chapter 12.

Transition State Theory

Transition state theory was proposed in 1935 by Henry Eyring, and further developed by Merrideth G. Evans and Michael Polanyi (Laidler & King, 1983), as another means of accounting for chemical reaction rates. It is based on the idea that a molecular collision that leads to reaction must pass through an intermediate state known as the transition state. For example, the reaction



would have an intermediate (ABC) where the B-C bond is partially broken, and the A-B bond is partially formed.



So the reaction is mediated by the formation of an activated complex (denoted with the double-dagger symbol ‡) and the decomposition of that complex into the reaction products. Using this theory, the rate of reaction can be expressed as the product of two factors

$$\text{rate} = (\text{transition state concentration}) \times (\text{decomposition frequency})$$

If the formation of the activated complex is considered to reach an equilibrium,

$$K^\ddagger = \frac{[ABC]^\ddagger}{[A][BC]}$$

So the concentration of the transition state complex can be expressed by

$$[ABC]^\ddagger = K^\ddagger [A][BC]$$

Using the relationship from Chapter 9 for the equilibrium constant, K^\ddagger can be expressed in terms of the free energy of formation of the complex (ΔG^\ddagger)

$$K^\ddagger = e^{-\frac{\Delta G^\ddagger}{RT}}$$

And so the reaction rate is given by

$$\text{rate} = (\text{frequency})[A][BC]e^{-\frac{\Delta G^\ddagger}{RT}}$$

and the remaining task is to derive an expression for the frequency factor. If the frequency is taken to be equal to the vibrational frequency for the vibration of the bond being broken in the activated complex in order to form the reaction products, it can be expressed in terms of the energy of the oscillation of the bond as the complex vibrates.

$$E = h\nu = k_B T$$

or

$$\nu = \frac{k_B T}{h}$$

The reaction rate is then predicted to be

$$\text{rate} = \frac{k_B T}{h} [A][BC] e^{-\frac{\Delta G^\ddagger}{RT}}$$

And the rate constant is thus given by

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

An alternative description gives the transition state formation equilibrium constant in terms of the partition functions describing the reactants and the transition state:

$$K^\ddagger = \frac{Q^\ddagger}{Q_A Q_{BC}} e^{-\frac{E_a^\ddagger}{RT}}$$

where Q_i is the **partition function** describing the i^{th} species. If the partition function of the transition state is expressed as a product of the partition function excluding and contribution from the vibration leading to the bond cleavage that forms the products and the partition function of that specific vibrational mode

$$Q^\ddagger = Q^{\ddagger'} q_v^\ddagger$$

In this case, q_v^\ddagger can be expressed by

$$q_v^\ddagger = \frac{1}{1 - e^{-\frac{h\nu^\ddagger}{k_B T}}} \approx \frac{k_B T}{h\nu^\ddagger}$$

So the equilibrium constant can be expressed

$$K^\ddagger = \frac{k_B T}{h\nu^\ddagger} \frac{Q^{\ddagger'}}{Q_A Q_{BC}} e^{-\frac{E_a^\ddagger}{RT}}$$

And so the rate constant, which is the product of n^\ddagger and K^\ddagger , is given by

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger'}}{Q_A Q_{BC}} e^{-\frac{E_a^\ddagger}{RT}}$$

which looks very much like the Arrhenius equation proposed quite a few years earlier! Thus, if one understands the vibrational dynamics of the activated complex, and can calculate the partition functions describing the reactants and the transition state, one can, at least in theory, predict the rate constant for the reaction.

In the next chapter, we will take a look at how kinetics studies can shed some light on chemical reaction mechanisms.

References

Arrhenius, S. A. (1889). Über die Dissociationswärme und den Einfluß der Temperatur auf den Dissociationsgrad der Elektrolyte. *Z. Phys. Chem.*, 4, 96-116.

Thermochemistry and Chemical Kinetics: Chemical Kinetics I © 2021 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

- House, J. E. (2007). *Principles of Chemical Kinetics* (2nd ed.). New York: Academic Press.
- Laidler, K., & King, M. C. (1983). Development of transition-state theory. *Journal of Physical Chemistry*, 87(15), 2657-2664.
- Lewis, W. C. (1918). Studies in catalysis. Part IX. The calculation in absolute measure of velocity constants and equilibrium constants in gaseous systems. *Journal of the Chemical Society, Transactions*, 113, 471-429.
- Progodich, R. V. (2014). A Stopped-Flow Kinetics Experiment for the Physical Chemistry Laboratory Using Noncorrosive Reagents. *Journal of Chemical Education*, 91(12), 2200-2202.
- Trautz, M. (1916). Das Gesetz der Reaktionsgeschwindigkeit und der Gleichgewichte in Gasen. Bestätigung der Additivität von $C_v-3/2R$. Neue Bestimmung der Integrationskonstanten und der Moleküldurchmesser. *Zeitschrift für anorganische und allgemeine Chemie*, 96(1), 1-28.

Vocabulary and Concepts

activation energy	266	order	254
Arrhenius prefactor	269	partition function.....	273
collisional cross section	268	rate law	253
exponential decay.....	257	reaction rate.....	251
first order rate law	256	stopped-flow method	252
half-life.....	263	Transition state theory.....	271
integrated rate law	255	zeroth order rate law	255
method of initial rates	261		

Learning Objectives

Problems