

## Chapter 49

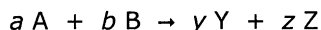
## WILL IT HAPPEN? Part 2

©2012, 2023 Mark E. Noble

We are still on the path seeking to find the answer to this question of "Will it happen?". Currently, our focus is the relationship between rate (speed) and the specific concentrations at some point in time.

## 49.1 At any rate

We continue with our generic reaction between reactants A and B.



Depending on the actual application, this equation may represent an elementary step or an overall composite of steps. Regardless, it is common that the rate (speed) of a reaction follows a function which can be represented as

$$\text{rate} = k [A]^f [B]^g$$

and this is called a rate law or rate equation. This rate is still equal to the prior speed relationships so, altogether, we can write

$$\text{rate} = k [A]^f [B]^g = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{y} \frac{\Delta[Y]}{\Delta t} = \frac{1}{z} \frac{\Delta[Z]}{\Delta t}$$

although for now we specifically focus on the rate law portion.

$$\text{rate} = k [A]^f [B]^g$$

The terms [A] and [B] in the rate law are now the actual concentrations at some time during the reaction; they are NOT the changes in concentration,  $\Delta[ ]$ , as used in the prior speed relationships. The concentration terms in rate laws can be expressed in various units, but we will primarily use mol/L which is the same as molarity for reactions in solution. It is common in kinetics to use concentrations for gases, although thermodynamics typically uses pressures for those. If you need to, you can still relate pressure and concentration by the ideal gas equation.

The symbols  $f$  and  $g$  in the rate law are exponents to the concentrations, and these are called orders: we say  $f$  is the order of A and  $g$  is the order of B. For example, if [A] is to the first power, then the rate law is first order in A. If [B] is to the second power, then this is second order in B. The rate law itself is said to have a total order equal to the sum of the individual orders,  $f + g$ .

The term  $k$  in the rate law is called the rate constant. It is a constant as long as the temperature is constant. (We'll change  $T$  later in the Chapter.) The units of  $k$  can vary. Every  $k$  will carry an inverse time unit such as per second,  $s^{-1}$ , or per minute,  $\text{min}^{-1}$ , or etc.; it may or may not also carry an inverse concentration unit. The concentration units for  $k$  can appear confusing at first but they work out so that the rate itself has units of concentration per time in all cases. Let's illustrate this for our generic rate law.

$$\text{rate} = k [A]^f [B]^g$$

For now, just watch the units. The unit for rate must come out in the end as concentration per time. [A] and [B] will each be in concentration units, and those units will be raised to the  $f$  and  $g$  power.

$$\frac{\text{conc}}{\text{time}} = k (\text{conc})^f (\text{conc})^g$$

Re-arranging, the units for  $k$  become

$$\frac{\text{conc}}{(\text{time}) (\text{conc})^f (\text{conc})^g}$$

and, since  $f + g = \text{total order}$ , then we can write this as

$$\frac{\text{conc}}{(\text{time}) (\text{conc})^{\text{total order}}}$$

which reduces to

$$\frac{\text{conc}^{(1 - \text{total order})}}{\text{time}}$$

or to the following.

$$\text{conc}^{(1 - \text{total order})} \text{time}^{-1}$$

The result of this is to show that the final units for  $k$  will depend on the total order.

- For first order,  $k$  has the simple unit of  $\text{time}^{-1}$ .
- For second order,  $k$  has the unit of  $\text{conc}^{-1} \text{time}^{-1}$ .
- For third order,  $k$  has the unit of  $\text{conc}^{-2} \text{time}^{-1}$ .
- Etc.

Since we are dealing with concentrations in mol/L, then inverse concentration can be written as  $(\text{mol/L})^{-1}$  or as L/mol. The latter version can appear strange at first. For example, for a third order process, the unit of  $k$  can be written  $(\text{mol/L})^{-2} \text{time}^{-1}$  or  $(\text{L/mol})^2/\text{time}$ . Be aware of the possible variations. This may all seem a bit tedious, but you will likely understand it better as you see it in use. Remember the bottom line:  $k$  will always take whatever units are necessary so that the units for the rate come out as concentration per time.

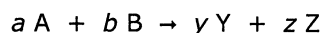
NOTA BENE!  $k$  is the rate constant. It is not the rate. Some people confuse rate constant  $k$  with the rate itself and it's easy to do since their names are similar. The rate is determined from the entire rate law which includes  $k$  along with one or more concentration terms and their orders. Different reactions can have the same rate but different values of  $k$  because the rate also depends on concentrations. Furthermore, orders can have a very big impact on rates. Let's say you run a reaction multiple times, changing the initial concentrations of reactants. Let's also say the reaction has the following rate law.

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

If you double the concentration of A for the reaction, then the rate doubles. If you double the concentration of B, however, then the rate quadruples ( $2^2$ ). These aspects become very useful when we want to make a reaction go faster: we simply use higher concentrations of those reactants which are present in the rate law, especially those with a higher order. In order to increase a concentration for a solute, you would use less solvent. In order to increase a concentration for a gas, you would use higher pressure of that gas.

The connection of the rate of the reaction to the concentration of one or more reagents lies in the notion of collisions, the importance of which was noted in the prior Chapter. A big factor which determines the rate of a reaction is the frequency of those collisions, which is the number of collisions per time between the particles involved. At higher concentrations, reactants will be closer together on average and will therefore be colliding more often; that will lead to more product being formed per time.

Rates for reactions can be measured experimentally, and this is how orders and rate constants are determined. This experimental information can then be used to support or refute our understanding of a mechanism for a particular process. The reason for this is that orders will connect to elementary steps, either directly or indirectly. The direct connection applies for a single elementary step: the orders in the rate law are the same as the coefficients in its balanced equation. This is an important connection to note. For example, if we propose that the equation

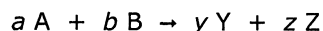


represents a single elementary step for a reaction, then we can write its rate law directly:

$$\text{rate} = k [\text{A}]^a [\text{B}]^b$$

The orders  $a$  and  $b$  can then be measured experimentally to support the proposal. If, however, the experimental orders prove to be other than  $a$  and/or  $b$ , then our proposed mechanism is wrong. By the way, the total order in a rate law for a single elementary step is also the molecularity of the step, so the total order can only be 1, 2 or 3. If the order is any other value, then it's not an elementary step.

For composite mechanisms, the overall rate law may not connect directly to the overall balanced equation. That's because an overall rate law is an algebraic composite of the individual elementary steps, and those cases can get complicated. For example, if the reaction



is the overall equation for a composite mechanism, then its rate law might end up as

$$\text{rate} = k [\text{A}]^f [\text{B}]^g$$

in which orders  $f$  and  $g$  bear no semblance to coefficients  $a$  or  $b$  in the overall equation. Or, the rate law might end up as

$$\text{rate} = k [\text{A}]^f$$

in which case reactant B is zero order, meaning its concentration has no effect on the rate. Or, the rate law might end up as

$$\text{rate} = k \frac{[\text{A}]^f [\text{B}]^g}{[\text{Y}]^h}$$

in which case product Y has a negative order (equal to  $-h$ ). There remain many other variations for composite rate laws and it just depends on the specific mechanism. By the way, we will not work with rate laws which have negative orders here. I just wanted to show you some of the possibilities.

Now would be a good time to note some distinctions between molecularity and order. Many students tend to confuse the terms. They have distinctly different definitions, but their numerical values can be the same or they can be different. As we continue, understanding the distinctions will be important.

- ▶ Molecularity is the number of particles reacting in an elementary step.
- ▶ An order is an exponent in a rate law as determined experimentally. That rate law could be for a single elementary step or for an overall composite reaction.
- ▶ The term molecularity only applies to single elementary steps; the values can only be 1, 2 or 3.
- ▶ Orders can apply to an elementary step or to an overall composite. The values for order can vary considerably for composite rate laws.
- ▶ For a single elementary step, the molecularity and the total order of the rate law will be the same, and this must be 1, 2 or 3.
- ▶ For the overall rate law of a composite series of reactions, the orders need not show any connection to the molecularity of any one step.

Let's now consider the specific rate laws for our two Examples from Chapter 48. For the First Example, the overall equation was

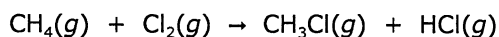


and you were told this is a simple mechanism. Thus, this equation is for the only elementary step. Since it is an elementary step we can write the rate law directly as

$$\text{rate} = k [\text{CH}_3\text{F}] [\text{Cl}^-]$$

in which the orders are the same as the coefficients in the balanced equation. This rate law has been confirmed experimentally. As indicated in the last Chapter, this is a bimolecular process. Since this is elementary, the molecularity and the total order are the same.

The Second Example



involved a composite mechanism so you cannot deduce anything about the overall rate law just from the overall equation. In actuality, the overall rate law is

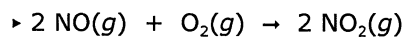
$$\text{rate} = k [\text{CH}_4] [\text{Cl}_2]^{1/2}$$

which means the reaction is first order in  $\text{CH}_4$  but one-half order in  $\text{Cl}_2$  for a total order of  $1\frac{1}{2}$ . As you can see, fractional orders are also possible in a composite rate law. This rate law can be derived from the rate laws for the individual elementary steps but such derivations will not be covered here.

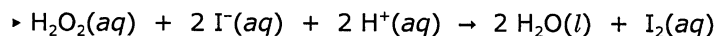
For illustration purposes, here are other equations from Chapter 48, now with their actual rate laws.



$$\text{rate} = k [\text{SO}_2\text{Cl}_2]$$



$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$$



$$\text{rate} = k [\text{H}_2\text{O}_2] [\text{I}^-] + k' [\text{H}_2\text{O}_2] [\text{I}^-] [\text{H}^+]$$

We noted in the last Chapter that the first two equations could be elementary or overall. (OK, since you've probably been wondering, I will tell you the first is an elementary step but the second is not.) We also said at that time that the third equation could not be elementary and it must be an equation for the overall reaction. As you can see by its rate law, overall rate laws can get a bit complicated.

You can do calculations with rate laws. You can do the rate law itself and you can connect this to the rates of changes for each product and reactant using the speed relationships. Let's do an example using the  $\text{SO}_2\text{Cl}_2$  reaction from above.

**Example 1.** For the following reaction,



the rate constant is  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ . What is the rate of the reaction when the concentration of  $\text{SO}_2\text{Cl}_2$  is 0.012 mol/L? What are the rates of change in the concentrations for each reactant and product?

The reaction rate is a straight plug-in.

$$\text{rate} = k [\text{SO}_2\text{Cl}_2] = 2.2 \times 10^{-5} \text{ s}^{-1} \times 0.012 \text{ mol/L} = 2.6 \times 10^{-7} \text{ (mol/L)/s}$$

That rate connects to the speed relationships

$$\text{rate} = 2.6 \times 10^{-7} \text{ (mol/L)/s} = -\frac{\Delta[\text{SO}_2\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{SO}_2]}{\Delta t} = \frac{\Delta[\text{Cl}_2]}{\Delta t}$$

which gives the following rates of change for the given condition.

$$\frac{\Delta[\text{SO}_2\text{Cl}_2]}{\Delta t} = -2.6 \times 10^{-7} \text{ (mol/L)/s}$$

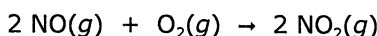
$$\frac{\Delta[\text{SO}_2]}{\Delta t} = 2.6 \times 10^{-7} \text{ (mol/L)/s}$$

$$\frac{\Delta[\text{Cl}_2]}{\Delta t} = 2.6 \times 10^{-7} \text{ (mol/L)/s}$$

Recall that a negative sign means the concentration is decreasing. The overall result is that the concentration of  $\text{SO}_2\text{Cl}_2$  is decreasing at the rate of  $2.6 \times 10^{-7} \text{ (mol/L)/s}$ , while the concentrations of  $\text{SO}_2$  and  $\text{Cl}_2$  are increasing at the rate of  $2.6 \times 10^{-7} \text{ (mol/L)/s}$ .

Here, you do one with a mix of coefficients.

**Example 2.** For the following reaction,



the rate constant is  $k = 7,100 \text{ (L/mol)}^2/\text{s}$ . What is the rate of the reaction when  $[\text{NO}] = 8.63 \times 10^{-4} \text{ mol/L}$  and  $[\text{O}_2] = 0.0150 \text{ mol/L}$ ? How fast are the concentrations changing for each reactant and product?

This equation and its rate law were given upstairs. Start with the rate law

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$$

and plug everything in.

You should get  $7.9 \times 10^{-5} \text{ (mol/L)/s}$  for the rate at the given conditions. This connects to the speed relationships as follows.

$$\text{rate} = 7.9 \times 10^{-5} \text{ (mol/L)/s} = -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

The concentration of NO is decreasing at the rate of  $16 \times 10^{-5} \text{ (mol/L)/s}$ , the concentration of  $\text{O}_2$  is decreasing at the rate of  $7.9 \times 10^{-5} \text{ (mol/L)/s}$ , and the concentration of  $\text{NO}_2$  is increasing at the rate of  $16 \times 10^{-5} \text{ (mol/L)/s}$ .

## 49.2 An integrated approach

As seen by the Examples above, we can calculate a rate at a given time for a specific amount of reactants. Often, however, the more important notion is how much reaction actually occurs in how much time. For example, if you start a reaction with 0.10 M of reactant in solution, how much time is needed for that reactant's concentration to reach 0.06 M? Or, if you start a reaction with 0.10 M reactant, what is its concentration after 2.0 h? These calculations derive from the rate laws but with a bit more calculus thrown in. We will not do the derivations, and we will simply proceed to the final results. These forms of equations are called integrated rate laws since they derive from calculus-based integration of the rate laws themselves.

There are different forms of these equations, based on the orders and stoichiometric coefficients for the reactants in the balanced equation. These can get very complex, so we will limit coverage to three basic Types.

- First Type: The reaction is first order in one (only) reactant, A.

This Type can be represented by the following generic equation.



If you are told the equation is an elementary step, then first order means the coefficient  $a$  must be 1. On the other hand, if the equation is not elementary, then  $a$  can be 1 or another number. In either case, since you are specifically told it is first order, then you can write the rate law as

$$\text{rate} = k [A]$$

and  $[A]$  is to the first power. Integration gives the first order, integrated rate law.

$$\ln \frac{[A]_0}{[A]_t} = akt$$

The subscripts on the concentrations  $[A]$  relate to time.  $[A]_0$  is the initial concentration at the start time of zero, and  $[A]_t$  is the concentration of A remaining after some time  $t$ . This equation is sometimes written in its exponential form

$$\frac{[A]_0}{[A]_t} = e^{akt}$$

and you should be able to work with either.

- Second Type: The reaction is second order in one (only) reactant, A.

This Type can be represented by the following generic equation.



If you are told the equation is elementary, then  $a = 2$  but, if the equation is not elementary, then  $a$  can be another number. Regardless, since you are specifically told second order, the rate law is

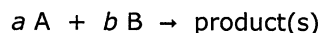
$$\text{rate} = k [A]^2$$

and integration gives the integrated rate law for second order.

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

- Third Type: The reaction is first order in each of two reactants, A and B, and second order overall.

This Type can be represented by the following generic equation.



If you are told the equation is elementary, then  $a = b = 1$  but, if the equation is not elementary, then the coefficients can be another number. Regardless, since you are told specifically that the reaction is first order in A and in B, then the rate law is the following.

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

This Type is very common, but the math for the integrated rate law can get quite complicated. The math simplifies substantially if we impose two conditions:  $a = b = 1$  and the initial concentrations of the reactants are equal,  $[A]_0 = [B]_0$ . If  $[A]$  and  $[B]$  start equally, and both A and B react in a 1:1 ratio, then

$[A]_t = [B]_t$  throughout the entire reaction. With these conditions, the derivation produces the same second order, integrated rate law as for the Second Type above,

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

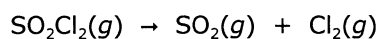
but now  $a = 1$  is a condition of the derivation. Since  $[A]_t = [B]_t$  at all times, then this equation is the same for both A and B.

In all three Types of our integrated rate law coverage, it is very important to note that the term  $[A]_t$  in the equations is the concentration of A which is still present in the system and has not yet reacted after time  $t$ . It is not the amount of A which has reacted and is gone. This detail sometimes causes confusion, so be careful. The amount of A which has actually reacted after some time  $t$  is  $[A]_0 - [A]_t$  and not  $[A]_t$  by itself.

Now for some illustrations.

The basic calculation using an integrated rate law is pretty much plug-and-chug. The value of  $a$  is the coefficient in the balanced equation. There're four other components:  $[A]_0$ ,  $[A]_t$ ,  $k$  and  $t$ ; if you are given three, then you can calculate the fourth. Just be sure to use the correct integrated rate law.

**Example 3.** For the reaction of  $\text{SO}_2\text{Cl}_2$  as cited previously,



if the reaction starts with  $[\text{SO}_2\text{Cl}_2] = 0.023 \text{ mol/L}$ , what concentration (in mol/L) remains after 4.1 hours?

The rate law was previously given as

$$\text{rate} = k [\text{SO}_2\text{Cl}_2]$$

and the rate constant was given as  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ . Since  $[\text{SO}_2\text{Cl}_2]$  is to the first power in the rate law, then this is first order and this falls under the First Type above. Set up that integrated rate law.

$$\frac{[A]_0}{[A]_t} = e^{akt}$$

Reactant A =  $\text{SO}_2\text{Cl}_2$  and its coefficient  $a$  in the balanced equation is one, so this becomes the following.

$$\frac{[\text{SO}_2\text{Cl}_2]_0}{[\text{SO}_2\text{Cl}_2]_t} = e^{kt}$$

The problem gives the initial  $[\text{SO}_2\text{Cl}_2]_0$  and you need to find  $[\text{SO}_2\text{Cl}_2]_t$  which still remains after  $t = 4.1 \text{ h}$ . Re-arrange.

$$[\text{SO}_2\text{Cl}_2]_t = \frac{[\text{SO}_2\text{Cl}_2]_0}{e^{kt}}$$

There will be a catch here in the  $kt$  part:  $k$  has the unit of  $\text{s}^{-1}$  but  $t$  was given in hours. The time units need to cancel (always!), so you need to convert h to s or s to h. The  $kt$  part becomes

$$kt = 2.2 \times 10^{-5} \text{ s}^{-1} \times 4.1 \text{ h} \times \frac{3600 \text{ s}}{\text{h}} = 0.3247\dots$$

and now the time units drop out. Plug in the whole thing.

$$[\text{SO}_2\text{Cl}_2]_t = \frac{0.023 \text{ mol/L}}{e^{0.3247\dots}}$$

You will get  $[\text{SO}_2\text{Cl}_2]_t = 0.017 \text{ mol/L}$ . That's the concentration of  $\text{SO}_2\text{Cl}_2$  which is still present after 4.1 h.

That's your basic calculation using an integrated rate law. Beyond this, there are some additional points to consider. For example, if you want to know the concentration of  $\text{SO}_2\text{Cl}_2$  which actually did react in 4.1 h, then that is the initial concentration minus the remaining concentration.

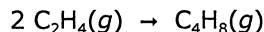
$$[\text{SO}_2\text{Cl}_2]_0 - [\text{SO}_2\text{Cl}_2]_t = 0.023 \text{ mol/L} - 0.017 \text{ mol/L} = 0.006 \text{ mol/L}$$

You might also want to know the concentration of a product which has formed after some time  $t$ . The concentration of product which has formed is stoichiometrically related to how much reactant has reacted,

and that relationship lies in the rxn ratios. In the present case, the balanced equation relates all reagents on a one-to-one mole-to-mole basis, which also means one-to-one in concentration. Thus, we can say that in the 4.1 h time, 0.006 mol/L  $\text{SO}_2\text{Cl}_2$  has reacted and this has produced 0.006 mol/L  $\text{SO}_2$  and 0.006 mol/L  $\text{Cl}_2$ .

Next.

**Example 4.** At high temperatures, ethylene,  $\text{C}_2\text{H}_4$ , can react to produce 1-butene,  $\text{C}_4\text{H}_8$ .



The reaction is second order in  $\text{C}_2\text{H}_4$  and  $k = 0.042 \text{ (L/mol)/min}$  at  $452 \text{ }^\circ\text{C}$ . For a reaction which starts with  $[\text{C}_2\text{H}_4]_0 = 0.00722 \text{ mol/L}$ , what is the concentration (in mol/L) of  $\text{C}_2\text{H}_4$  after 720. min? What will be the concentration (in mol/L) of  $\text{C}_4\text{H}_8$  at that time?

This problem asks for two concentrations after 720. min: one for the amount of reactant which remains and one for the amount of product which has formed. The integrated rate laws deal with reactant concentrations, so we can find  $[\text{C}_2\text{H}_4]_t$  from that. Then, we can find the concentration of  $\text{C}_4\text{H}_8$  which has formed using standard stoichiometric relationships.

You are told the process is second order, so you want the second order, integrated rate law for one reactant (Second Type).

$$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = akt$$

The coefficient on  $\text{C}_2\text{H}_4$  is two in the balanced equation.

$$\frac{1}{[\text{C}_2\text{H}_4]_t} - \frac{1}{[\text{C}_2\text{H}_4]_0} = 2kt$$

We seek  $[\text{C}_2\text{H}_4]_t$ ; re-arrange.

$$\frac{1}{[\text{C}_2\text{H}_4]_t} = 2kt + \frac{1}{[\text{C}_2\text{H}_4]_0}$$

Plug in the given info and solve. (Watch the sigfig business.)

$$\begin{aligned} \frac{1}{[\text{C}_2\text{H}_4]_t} &= 2 \times \frac{0.042 \text{ L}}{\text{mol} \cdot \text{min}} \times 720. \text{ min} + \frac{1}{0.00722 \text{ mol/L}} \\ &= \underbrace{60. \text{ L/mol}} + \underbrace{139 \text{ L/mol}} \end{aligned}$$

This gives

$$\frac{1}{[\text{C}_2\text{H}_4]_t} = 199 \text{ L/mol}$$

and inversion of that gives the concentration of  $\text{C}_2\text{H}_4$  which remains after 720. min.

$$[\text{C}_2\text{H}_4]_t = 0.00503 \text{ mol/L}$$

That's the first answer.

For the concentration of  $\text{C}_4\text{H}_8$  product which has formed, we need the concentration of  $\text{C}_2\text{H}_4$  which has actually reacted.

$$[\text{C}_2\text{H}_4]_{\text{reacted}} = [\text{C}_2\text{H}_4]_0 - [\text{C}_2\text{H}_4]_t = 0.00722 \text{ mol/L} - 0.00503 \text{ mol/L} = 0.00219 \text{ mol/L}$$

The concentration of  $\text{C}_2\text{H}_4$  which has reacted then relates to the amount of  $\text{C}_4\text{H}_8$  which has been produced by way of the usual stoichiometry rxn ratio, using the coefficients from the balanced equation. Although we have previously used moles for a rxn ratio, we can use concentrations here because both gases are in the same volume. So the rxn ratio is

$$\frac{1 \text{ (mol } \text{C}_4\text{H}_8\text{/L)}}{2 \text{ (mol } \text{C}_2\text{H}_4\text{/L)}}$$

and the stoichiometry "string" is simply

$$0.00219 \text{ (mol C}_2\text{H}_4\text{/L)} \times \frac{1 \text{ (mol C}_4\text{H}_8\text{/L)}}{2 \text{ (mol C}_2\text{H}_4\text{/L)}} = 0.00110 \text{ (mol C}_4\text{H}_8\text{/L)}$$

and that's the concentration of C<sub>4</sub>H<sub>8</sub> which has been produced after 720. min. End of problem.

Another variation to these problems deals with the fraction or percent of reactant which remains after some time. The fraction remaining after some time is given by

$$\text{fraction remaining} = \frac{[A]_t}{[A]_0}$$

and the percent remaining is this value converted to a percent.

$$\text{percent remaining} = \frac{[A]_t}{[A]_0} \times 100\%$$

A related parameter is the percent completion or percent reaction. This is based on how much reactant has already reacted.

$$\text{percent completion or percent reaction} = \frac{[A]_0 - [A]_t}{[A]_0} \times 100\%$$

For the present Example 4, the percent remaining after 720. min is

$$\text{percent remaining} = \frac{0.00503 \text{ mol/L}}{0.00722 \text{ mol/L}} \times 100\% = 69.7\%$$

and the percent completion is the following.

$$\text{percent completion} = \frac{0.00219 \text{ mol/L}}{0.00722 \text{ mol/L}} \times 100\% = 30.3\%$$

(You could also find the percent completion by simple subtraction, 100.0% – 69.7%.) These parameters are useful as a general, relative indicator of how much of the reaction has or has not occurred. In this case, we can say the reaction is only 30.3% complete after 720. min.

From the calculations so far, you can see that the integrated rate laws can tell us how much reactant remains after some given amount of time, and that can lead to how much reactant has reacted or how much product has been made. Now let's turn this around: you can also calculate the amount of time needed to reach a certain point in the reaction. Here's an Example which you can do.

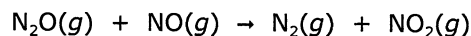
.....  
**Example 5.** The conditions given for Example 4 resulted in 69.7% C<sub>2</sub>H<sub>4</sub> remaining after 720. min. How many minutes are required for 50.0% to remain?  
 .....

50.0% remaining after time *t* means [C<sub>2</sub>H<sub>4</sub>]<sub>*t*</sub> = 0.500 [C<sub>2</sub>H<sub>4</sub>]<sub>0</sub>. Plug the various values into the integrated rate law and solve for *t*.

You can check your answer in Example 7 below.

OK, now for the Third Type.  
 .....

**Example 6.** The following reaction is first order in each reactant.



At 1,100 K, *k* = 18.6 (L/mol)/s. For a reaction which starts with [N<sub>2</sub>O]<sub>0</sub> = [NO]<sub>0</sub> = 2.52 × 10<sup>-4</sup> mol/L, what concentration (in mol/L) of each reactant remains after 50.0 min?  
 .....

We need the second order, integrated rate law with *a* = 1.



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

We'll just stick with using A here, since [A] is the same for both N<sub>2</sub>O and NO over all times of the reaction. Re-arrange, plug in and solve for [A]<sub>t</sub>. Watch the units for time.

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

$$\frac{1}{[A]_t} = \frac{18.6 \text{ L}}{\text{mol} \cdot \text{s}} \times \underbrace{50.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}}}_{55,800 \text{ L/mol}} + \frac{1}{2.52 \times 10^{-4} \text{ mol/L}} + 3,970 \text{ L/mol}$$

This becomes

$$\frac{1}{[A]_t} = 59,800 \text{ L/mol}$$

which is then inverted to give the concentration of A which remains after 50.0 min.

$$[A]_t = 1.67 \times 10^{-5} \text{ mol/L}$$

Thus,

$$[\text{N}_2\text{O}]_t = [\text{NO}]_t = 1.67 \times 10^{-5} \text{ mol/L}$$

and you're done.

### 49.3 Two halves do not make a whole.

The prior Example 5 serves to illustrate a very useful parameter in kinetics studies which is called half-life, symbolized  $t_{1/2}$ . A half-life is a time period: it is the time required for one half of the initial amount of a reactant to react, which also means one half of the initial amount remains. This term can cause confusion, however, since it's not one-half the time of the total life of the reaction. It's only for one time interval which begins with some amount of [A] and ends up at 50% of that. For example, let's say you have a reaction in solution beginning with [A]<sub>0</sub> originally at 1 M.

The first half-life interval starts with [A] = 1 M and ends when [A] = (1/2) M.

The second half-life interval starts at (1/2) M and ends at (1/4) M.

The third half-life interval starts at (1/4) M and ends at (1/8) M.

Etc.

Each subsequent half-life interval begins where the prior one ended and it then goes to one-half of that amount of A. Thus, two half-lives do not equal one whole life; the second half-life ends when one-fourth of the original amount of A remains. Since one-fourth remains, then the reaction is three-fourths (75%) completed after two half-lives. Relative to the original [A]<sub>0</sub> at the very start of the reaction, there is a power relationship for the amount remaining after each half-life.

The first half-life ends at (1/2)<sup>1</sup> [A]<sub>0</sub>, or when 50% of the original [A]<sub>0</sub> remains. This corresponds to 50% completion.

The second half-life ends at (1/2)<sup>2</sup> [A]<sub>0</sub>, or when 25% of the original [A]<sub>0</sub> remains. This corresponds to 75% completion.

The third half-life ends at (1/2)<sup>3</sup> [A]<sub>0</sub>, or when 12.5% of the original [A]<sub>0</sub> remains. This corresponds to 87.5% completion.

Etc.

In general, after  $n$  half-lives, the amount of A remaining is (1/2) <sup>$n$</sup>  times the original [A]<sub>0</sub>.

Calculations for half-lives can be derived from the integrated rate laws. For the derivations, the time  $t$  is  $t_{1/2}$  and, at that time, [A]<sub>t</sub> = (1/2) [A]<sub>0</sub>.

- First order (First Type)

$$\ln \frac{[A]_0}{[A]_t} = akt_{1/2} = \ln \frac{[A]_0}{(1/2) [A]_0}$$

The [A]<sub>0</sub> terms cancel on the right and you have

$$akt_{1/2} = \ln 2$$

which gives the following result.

$$t_{1/2} = \frac{\ln 2}{ak}$$

- Second order (Second and Third Types)

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt_{1/2} = \frac{1}{(1/2)[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

(For the Third Type,  $a$  is still one within our coverage.) The  $[A]_0$  term does not cancel for these. Rearranging gives the following.

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

A notable difference between the first and second order results is that the second order half-life depends on the concentration  $[A]_0$  whereas that term dropped out of the derivation for the first order half-life. Regardless, calculations using the half-life equations are pretty much plug-and-chug. Let's return to the two problems used previously in the integrated rate laws.

**Example 7.** Calculate the half-life (in s) for the  $\text{SO}_2\text{Cl}_2$  reaction in Examples 1 (and 3), and the half-life (in min) for the  $\text{C}_2\text{H}_4$  reaction in Example 4.

The reaction for  $\text{SO}_2\text{Cl}_2$  was first order.

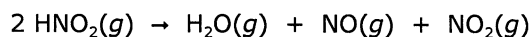
$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693147\dots}{1 \times 2.2 \times 10^{-5} \text{ s}^{-1}} = 32,000 \text{ s}$$

The reaction for  $\text{C}_2\text{H}_4$  was second order. You had already found the half-life indirectly in Example 5; now you can check that answer by straight plug-in.

$$t_{1/2} = \frac{1}{ak[A]_0} = \frac{1}{2 \times 0.042 \text{ (L/mol)/min} \times 0.00722 \text{ mol/L}} = 1,600 \text{ min}$$

Your turn.

**Example 8.** In the gas phase, nitrous acid can react according to the following equation.



The rate law is

$$\text{rate} = k [\text{HNO}_2]^2$$

and  $k = 110. \text{ (L/mol)/s}$  at  $400. \text{ }^\circ\text{C}$ . For these conditions, find the half-life (in s) of the reaction which starts with  $[\text{HNO}_2] = 1.37 \times 10^{-5} \text{ mol/L}$ .

You need an equation for half-life, but for what order? The balanced equation gives no clue since you are not told whether it is elementary or not. On the other hand, the rate law does tell you that the reaction is second order in  $\text{HNO}_2$ . Take it from there.

Your answer is 332 s.

That's enough for  $t$ . Now it's time for  $T$ .

#### 49.4 $k$ and $T$

As temperature increases, reactions typically go faster and need less time. This is reflected in the value of the rate constant,  $k$ , which increases as  $T$  goes up. Why? It's got to do with the thermal energy in the system and the activation energy of the reaction itself.

As  $T$  increases, there's more thermal energy in the system and this increases motions. Particles are moving faster on average. As a result, collisions occur more often and with more energy. The "more often" part increases the rate constant somewhat, but it is not the major effect. The "more energy" part has the bigger effect. As particles collide with more energy, more collisions will have enough energy to reach the transition state and to get over the energy barrier. The relationship which links the rate constant and temperature is commonly given as an exponential function.

$$k = A e^{-E_a/RT}$$

Historically, this is called the Arrhenius equation. This is an approximate equation but it does give decent results and it is very simple to use; better equations are known but those get more complicated. Notice that  $E_a$  and  $T$  appear in an exponent as a ratio. Furthermore, there's a negative sign on the exponent which gives an inverse effect. Let's rewrite this as follows.

$$k = A e^{-E_a/RT} = \frac{A}{e^{E_a/RT}}$$

Here's how this works.

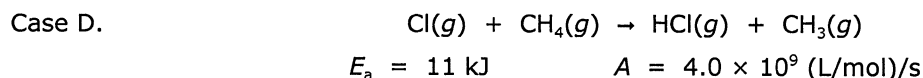
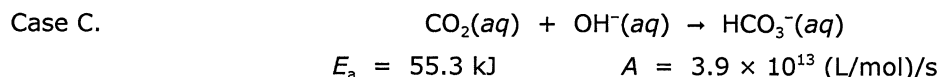
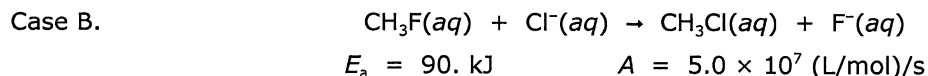
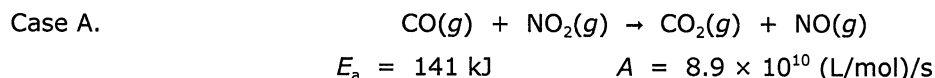
Conceptually, for a reaction with a higher activation energy, the reaction should go slower because fewer collisions will meet the demand of the higher energy barrier. This is reflected in the above equation: the denominator term  $e^{E_a/RT}$  will be larger and  $k$  will therefore be smaller.

Conceptually, for a reaction at higher temperature, the reaction should go faster because there is more energy in the system and a greater proportion of collisions will meet or exceed the energy barrier. In the above equation, the term  $e^{E_a/RT}$  will be smaller and  $k$  will be larger.

Again, keep in mind that  $k$  itself is not speed:  $k$  and concentrations determine speed. However, for a given set of concentrations, if we could decrease  $E_a$  and/or if we could increase  $T$ , then  $k$  would be larger and the reaction would be faster. Unfortunately,  $E_a$  is determined by the mechanism so we cannot change  $E_a$  unless we change the mechanism. On the other hand, we can change  $T$ .

What about the  $R$  and the  $A$ ?  $R$  is again the gas constant in units of 8.314 J/K.  $A$  is something new; it's given the unimpressive name of "the pre-exponential factor" because it comes before the exponential term in the original equation. It is an experimental constant which incorporates a variety of factors but these are difficult to separate out exactly. (The orientation of collision is one of the factors covered by  $A$ .) Notice that  $k$  depends directly on  $A$ : as  $A$  increases, then  $k$  increases proportionally and vice versa. The units of  $A$  will be the same as the units of  $k$ ; the exponential term carries no units because the units within  $E_a/RT$  cancel out.

Over the years, many values of  $A$  and of  $E_a$  have been determined for many kinds of reactions. Here are several Cases.



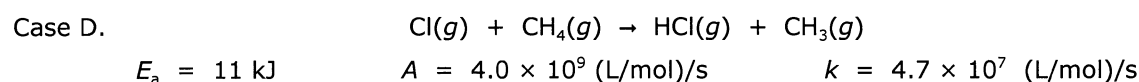
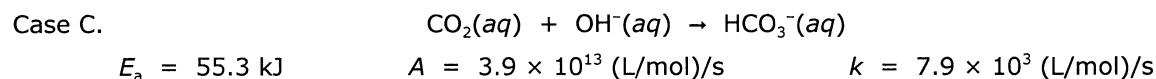
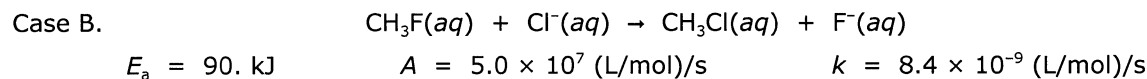
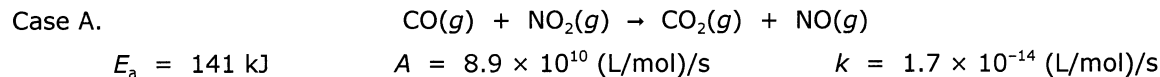
For purposes of calculating  $k$  from  $E_a$  and  $A$ , you have to be careful with the units in the  $-E_a/RT$  part:  $E_a$  is typically in kJ's but  $RT$  is typically in J's. Here's how that works at 25 °C for Case A, after converting  $E_a$  to J's.

$$\frac{-E_a}{RT} = \frac{-141,000 \text{ J}}{(8.314 \text{ J/K})(298 \text{ K})} = -56.9105\dots$$

Don't round off yet. Plug that in for  $k$ .

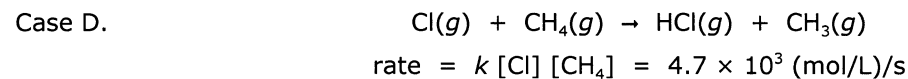
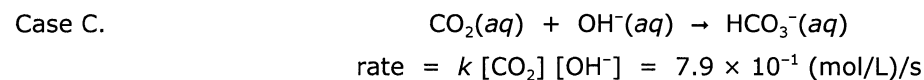
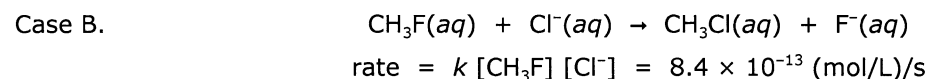
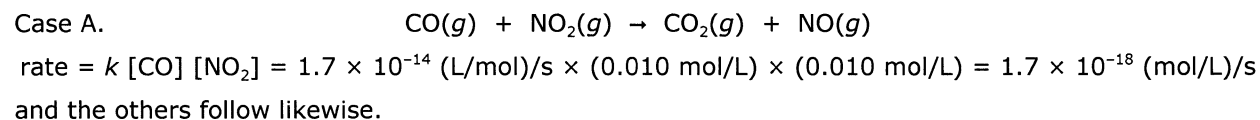
$$k = A e^{-E_a/RT} = 8.9 \times 10^{10} \text{ (L/mol)/s} \times e^{-56.9105\dots} = 1.7 \times 10^{-14} \text{ (L/mol)/s}$$

Doing this for each Case above gives the following results (which you should be able to confirm).



These four Cases are listed from lowest  $k$  to highest  $k$ . They are also listed from highest  $E_a$  to lowest  $E_a$ . That correspondence won't be true for all comparisons of reactions, however, because  $A$  can also have an effect. Notice here that the  $A$  values do not fit a trend. In general,  $E_a$  dominates the calculation for  $k$  but  $A$  can sometimes throw off a trend between  $E_a$  and  $k$ . Typical values for  $A$  range from  $10^8$  to  $10^{15}$  but those values also depend on the order of the reaction. Typical values for  $E_a$  range from zero or so into the several hundred kJ range. Any reaction with  $E_a$  in the 120 - 140 kJ range and higher is not doing much at room temperature in a reasonable time because the barrier is simply too high.

All four Cases above are second order elementary reactions, first order in each reactant. As such, all will have a rate law of rate =  $k [A] [B]$ . If all four reactions were run starting with the same concentration of reactants, then the sequence listed is slowest to fastest. To illustrate, let's say we start all of the reactions with 0.010 mol/L for each reactant. The rates are calculated as

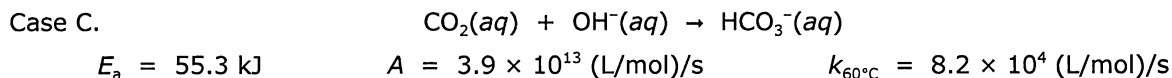
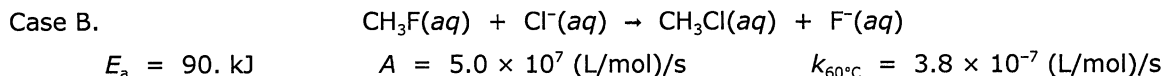


These results span  $10^{21}$  in rates. Case A is basically not happening even though it is exergonic. Its first half-life is  $1.9 \times 10^8$  years; hundreds of millions of years might be OK in geochemistry but not in the laboratory, so, for all practical purposes, this reaction does not happen. Case B isn't too swift either but its first half life is only 3.8 centuries. On the other hand, the first half-life for Case C is 13 milliseconds and that for Case D is 2.1 microseconds. Quite a comparison, eh?

But all of those are at 25 °C. Let's start cooking.

At higher temperatures with more thermal energy in the system, reactions speed up. The Arrhenius equation allows a calculation of rate constants at various temperatures, assuming that  $E_a$  and  $A$  do not change with  $T$ . This assumption proves to be OK over a range of several hundred degrees for many reactions, and we will adopt that assumption here. Besides, for a reaction in solution, the temperature range is much narrower, somewhere between the freezing point and the boiling point of the solution.

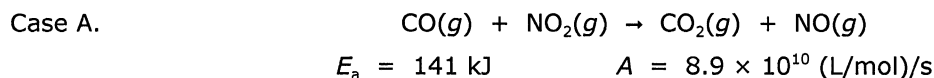
The calculation of  $k$  at other temperatures is just a plug-in using Arrhenius. Cases B and C above are aqueous solution reactions; here are their rate constants calculated for 60. °C.



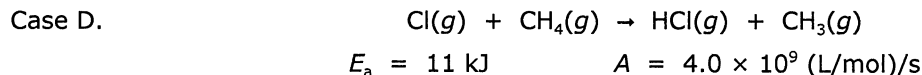
Compare these to the previous values at 25 °C. The  $k$  value for Case B increased 45-fold while the  $k$  value for Case C increased 10.-fold. The different size of the effect is due to the different  $E_a$  values:  $T$  effects are larger when  $E_a$  is larger. For more examples, let's cook up Cases A and D.

.....  
**Example 9.** Find the rate constants for Cases A and D at 225 °C.  
 .....

Plug in.



$$k_{225^\circ\text{C}} = A e^{-E_a/RT} =$$



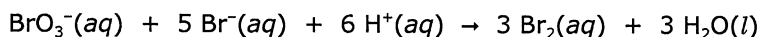
$$k_{225^\circ\text{C}} = A e^{-E_a/RT} =$$

If you compare these to the prior values at 25 °C, you will find that  $k$  for Case A increases 8.2-billion-fold while the  $k$  for Case D increases a mere 6.0-fold. Again, temperature effects are larger when  $E_a$  is larger and the  $E_a$  values for these two Cases are very different.

With that, we rest our Cases.

## Problems

- True or false.
  - Every mechanism with only one elementary step is first order (overall).
  - The rate constant,  $k$ , for a third order process has the units of  $\text{conc}^{-2} \text{ time}^{-1}$ .
  - All second order reactions are bimolecular.
  - After two half-lives, one-fourth of the initial amount of reactant remains.
  - A faster reaction will always have a longer half-life.
  - Reactions are generally faster when the activation energy is greater.
  - Reactions are generally faster when the temperature is higher.
  - As  $E_a$  increases,  $k$  decreases.
- Consider the following balanced equation.

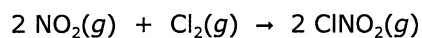


The rate law for this reaction is the following.

$$\text{rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

Indicate whether each statement below is true or false.

- The reaction is fourth order overall.
  - The reaction is zero order in bromide.
  - The balanced equation as shown is the single elementary step.
  - The rate will be faster by a factor of two if  $[\text{H}^+]$  is doubled.
  - The rate will be faster by a factor of two if  $[\text{BrO}_3^-]$  is doubled.
3. Consider the following balanced equation.

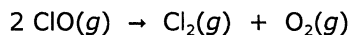


The rate law for this reaction is the following.

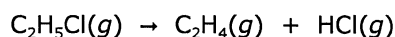
$$\text{rate} = k [\text{Cl}_2] [\text{NO}_2]^2$$

Indicate whether each statement below is true or false.

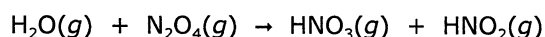
- The reaction is first order in chlorine.
  - The reaction is third order overall.
  - The rate will be slower by a factor of two if the concentration of  $\text{Cl}_2$  is doubled.
  - The rate will be faster by a factor of four if the concentration of  $\text{NO}_2$  is doubled.
4. The following reaction represents an elementary step.



- Write the rate law.
  - At some point in time, if the rate of the reaction is  $1.0 \times 10^{-5}$  (mol/L)/s, how fast are the concentrations changing for the reactant and each product?
5. The following reaction is first order in  $\text{C}_2\text{H}_5\text{Cl}$ ;  $k = 4.7 \text{ s}^{-1}$  at 960. K.



- Write the rate law.
  - What is the rate of the reaction (in (mol/L)/s) when  $[\text{C}_2\text{H}_5\text{Cl}] = 0.089$  mol/L?
  - What is the half-life (in s) of the reaction?
6. The following reaction is first order in each reactant.



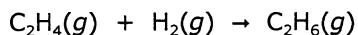
- Write the rate law.
  - If the rate of the reaction is  $1.08 \times 10^{-4}$  (mol/L)/s at 298 K when  $[\text{H}_2\text{O}] = 4.16 \times 10^{-4}$  mol/L and  $[\text{N}_2\text{O}_4] = 3.24 \times 10^{-4}$  mol/L, what is the value of  $k$  (in (L/mol)/s)?
7. The following reaction is second order in  $\text{NO}_2$ ;  $k = 0.68$  (L/mol)/s at 500 K.



The reaction begins with  $[\text{NO}_2] = 0.0345$  mol/L.

- What is the half-life (in s)?  
After 6.6 s,
- what concentration (in mol/L) of  $\text{NO}_2$  remains?
- what concentration (in mol/L) of  $\text{NO}$  has formed?
- what is the percent completion?

8. The following reaction is first order in each reactant, with  $k = 1.10 \text{ (L/mol)/s}$  at 873 K.



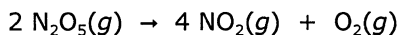
The reaction begins with  $[\text{C}_2\text{H}_4] = [\text{H}_2] = 1.70 \times 10^{-4} \text{ mol/L}$ .

- a. What is the half-life (in s)?

After 30.0 min,

- b. what concentration (in mol/L) of  $\text{C}_2\text{H}_4$  remains?  
c. what concentration (in mol/L) of  $\text{C}_2\text{H}_6$  has formed?  
d. what is the percent completion?

9. The following reaction is first order in  $\text{N}_2\text{O}_5$ ;  $t_{1/2} = 0.29 \text{ s}$  at 325 K.



The reaction begins with  $[\text{N}_2\text{O}_5] = 0.026 \text{ mol/L}$ . After 0.20 s,

- a. what concentration (in mol/L) of  $\text{N}_2\text{O}_5$  remains?  
b. what concentration (in mol/L) of  $\text{NO}_2$  has formed?  
c. what is the percent completion?

10. For the following reaction,  $E_a = 252 \text{ kJ}$  and  $A = 9.12 \times 10^{12} \text{ s}^{-1}$ .



Calculate the rate constant (in  $\text{s}^{-1}$ ) at 1,300. K.