

## Chapter 49

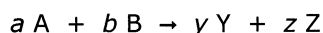
## WILL IT HAPPEN? Part 2

© 2012 Mark E. Noble  
noblereaction.org

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 equation. It is common that the rate (speed) of such 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 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 focus on the rate law portion.

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

The terms  $[A]$  and  $[B]$  in the rate law are 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 also molarity, M, for solutions). It is common in kinetics to use concentrations for gases, although thermodynamics typically uses pressures for those. Despite that difference, 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 re-arranges 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.

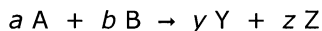
Since we are dealing with concentrations in mol/L, then inverse concentration can be written as  $(\text{mol/L})^{-1}$  or as L/mol. The latter version can appear strange at first. For example, for a third order process, the unit of  $k$  can be written  $(\text{mol/L})^{-2} \text{time}^{-1}$  or  $(\text{L/mol})^2/\text{time}$ . 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.

**IMPORTANT POINT.**  $k$  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 have the following rate law.

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

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.

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 disprove 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

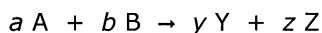


represents a single elementary step for a reaction, then we can write its rate law directly as

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

and this rate law can be confirmed experimentally. On the other hand, if the experimental orders disagree, 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 so directly to the overall balanced equation. That's because an overall rate law is an algebraic composite of the individual 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

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

in which  $f$  and  $g$  bear no semblance to  $a$  or  $b$ ; or, the rate law might end up as

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

in which reactant B is zero order and its concentration has no effect on the rate; or, the rate law might end up as

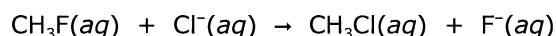
$$\text{rate} = k \frac{[A]^f [B]^g}{[Y]^h}$$

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 values can be the same. As we continue, understanding the distinctions will be important.

- ▶ The molecularity is the number of particles reacting in an elementary step.
- ▶ An order is an exponent in an experimental rate law. That rate law could be for an elementary step or for an overall 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 mechanism. The values for order can vary considerably for composites.
- ▶ 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 at all to the molecularity of any one step. In these cases, an order can be any number.

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

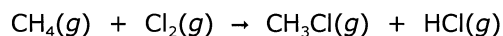


and you were told this is a simple mechanism. Thus, this equation is for the only elementary step. Since it is an elementary step and since the coefficients are one each on  $\text{CH}_3\text{F}$  and  $\text{Cl}^-$ , you can say the reaction is first order in  $\text{CH}_3\text{F}$  and first order in  $\text{Cl}^-$ . The rate law is then

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

and 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

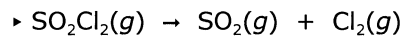


involved a composite mechanism so you cannot deduce anything about the overall rate law just from the overall equation. In actuality, the overall rate law is

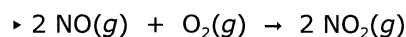
$$\text{rate} = k [\text{CH}_4] [\text{Cl}_2]^{1/2}$$

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 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.

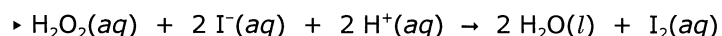
For illustration purposes, here are other equations from Chapter 48, now with their actual rate laws.



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



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



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

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 that third entry, the overall rate law for a composite process can get complicated.

You can do calculations with rate laws. Let's do an example using the  $\text{SO}_2\text{Cl}_2$  reaction.

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



the rate constant is  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ . What is the speed of the reaction when the concentration of  $\text{SO}_2\text{Cl}_2$  is 0.012 mol/L?

This 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 speeds for the given condition.

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

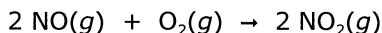
$$\frac{\Delta[\text{SO}_2]}{\Delta t} = 2.6 \times 10^{-7} \text{ (mol/L)/s}$$

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

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  $k = 7100 \text{ (L/mol)}^2/\text{s}$ . What is the speed of the reaction when  $[\text{NO}] = 8.63 \times 10^{-4} \text{ mol/L}$  and  $[\text{O}_2] = 0.0150 \text{ mol/L}$ ?

This is the middle equation from above. Get 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  $\text{O}_2$  is decreasing at the rate of  $7.9 \times 10^{-5} \text{ (mol/L)/s}$ , the concentration of  $\text{NO}$  is decreasing at the rate of  $16 \times 10^{-5} \text{ (mol/L)/s}$ , 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 0.02 M? Or, if you start a reaction with 0.10 M reactant, what is the 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 relationships for the reactants in the balanced equation. These can get very complex, so we will limit the coverage to the two simplest cases, and those involve only one reactant A. The two cases are first-order in A and second-order in A. We will not do integrated versions for rate laws which include other reactants.

Consider a reaction which is first order in A and for which a general balanced equation is



If the equation is for an elementary step, then first order means the coefficient  $a$  must be 1. On the other hand, if the equation is for an overall equation, then  $a$  can be 1 or another number. In either case, since it's first order, then you can write the rate law as

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

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

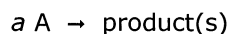
$$\ln \frac{[A]_0}{[A]_t} = akt$$

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.

Now consider a reaction which is second order in A and for which the balanced equation is represented by the following.



If the equation is elementary, then  $a = 2$  but, if the equation is overall, then  $a$  can again be otherwise. Regardless, since it's second order, the rate law is

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

and integration gives the integrated rate law for second order

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

**IMPORTANT POINT!** The term  $[A]_t$  in these equations is the concentration of A which is present in the system and still remains after time  $t$ . It is not the amount of A which has reacted and is gone. This detail sometimes causes confusion, so keep this in mind. 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, first order or second order. Here's an example.

**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 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 is  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$ . Since  $[\text{SO}_2\text{Cl}_2]$  is to the first power in the rate equation, then this is first order; you want the first order version of the integrated rate law. The coefficient of  $\text{SO}_2\text{Cl}_2$  is one in the balanced equation so we use

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

Now figure out what you have and what you need. The problem gives initial  $[\text{SO}_2\text{Cl}_2]_0 = 0.023 \text{ mol/L}$  and it asks for  $[\text{SO}_2\text{Cl}_2]_t$  at  $t = 4.1 \text{ h}$ .

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

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 will need to cancel, so you need to convert h to s. 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 the units drop out. Now 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 remains after 4.1 h.

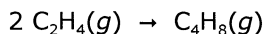
That's your basic calculation using an integrated rate law. Beyond this, there are some additional points to consider. For example, if you want to know the concentration of  $\text{SO}_2\text{Cl}_2$  which actually did react in 4.1 h, then that is

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

You might also want to know an amount of product which has formed after some time  $t$ . The amount 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 by a one-to-one mole-to-mole relationship, 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  $\text{Cl}_2$ . You can solve for moles, too. Since these are concentrations, you would need to know volume. You can even calculate pressures if you know the temperature.

Let's try a different example.

**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 of  $\text{C}_2\text{H}_4$  after 720. min? What will be the concentration 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 the  $[\text{C}_2\text{H}_4]$  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. The coefficient on  $\text{C}_2\text{H}_4$  is two in the balanced equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt = 2 kt$$

We seek  $[C_2H_4]_t$ ; re-arrange.

$$\frac{1}{[C_2H_4]_t} = 2 kt + \frac{1}{[C_2H_4]_0}$$

Solve.

$$\frac{1}{[C_2H_4]_t} = 2 \times \frac{0.042 \text{ L}}{\text{mol} \cdot \text{min}} \times 720. \text{ min} + \frac{1}{0.00722 \text{ mol/L}}$$

$$\frac{1}{[C_2H_4]_t} = 60. \text{ L/mol} + 139 \text{ L/mol} = 199 \text{ L/mol}$$

Invert that to get 0.00503 mol/L; that's the concentration of  $C_2H_4$  which remains. That's the first answer.

For the concentration of  $C_4H_8$  which has formed, we need the concentration of  $C_2H_4$  which has actually reacted.

$$[C_2H_4]_{\text{reacted}} = [C_2H_4]_0 - [C_2H_4]_t = 0.00722 \text{ mol/L} - 0.00503 \text{ mol/L} = 0.00219 \text{ mol/L}$$

That relates to the amount of  $C_4H_8$  which has been produced by way of the usual rxn ratio, using the coefficients from the balanced equation. Although we typically use moles for a rxn ratio, we can use concentrations here because both gases are in the same volume.

$$0.00219 \text{ (mol } C_2H_4/L) \times \frac{1 \text{ (mol } C_4H_8/L)}{2 \text{ (mol } C_2H_4/L)} = 0.00110 \text{ (mol } C_4H_8/L)$$

That's your answer for the concentration of  $C_4H_8$  product. End of problem.

Another variation to these problems deals with the fraction or percent 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.

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

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

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

Let's illustrate these calculations using the results for 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 given by

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

This says that the reaction is only 30.3% complete after 720. min.

Now a different twist: the integrated rate laws also allow you to calculate how much time is required for some amount of reaction. That will use the same equations as above, just solving for  $t$  instead of  $[A]_t$ . Here's an Example which you can do.

.....  
**Example 5.** The conditions given for Example 4 gave 30.3% reaction after 720. min. How many minutes are required for 50.0% reaction?  
 .....

You'll need  $[C_2H_4]_0$  and  $k$  from above. For 50.0% reaction, you set  $[C_2H_4]_t = 50.0\%$  of  $[C_2H_4]_0$ . Plug these into the second order integrated rate law and solve for  $t$ .

You can check your answer in Example 6 below.

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

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 period which is needed for one half of the amount of a reactant to react. 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 period beginning with some amount of  $[A]$  and ending up at 50% of that. For example, let's say you have a reaction in solution beginning with  $[A]_0$  originally at 1 M.

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

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

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

Etc.

Each subsequent half-life period 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  $[A]_0$  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  $(1/2)^1 [A]_0$ , or when 50% of the original  $[A]_0$  remains. This corresponds to 50% completion.

The second half-life ends at  $(1/2)^2 [A]_0$ , or when 25% of the original  $[A]_0$  remains. This corresponds to 75% completion.

The third half-life ends at  $(1/2)^3 [A]_0$ , or when 12.5% of the original  $[A]_0$  remains. This corresponds to 87.5% completion.

Etc.

In general, after  $n$  half-lives, the amount of A remaining is  $(1/2)^n$  times the original  $[A]_0$ .

Calculations for half-lives can be derived from the integrated rate laws. For the derivations, the time  $t$  is set to  $t_{1/2}$  and, at that time,  $[A]_t = (1/2) [A]_0$ .

► First order

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

The  $[A]_0$  terms cancel and you have

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

which gives the following result.

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

► Second order

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

The  $[A]_0$  term does not cancel for these. Re-arranging 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 starting 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 equations.

**Example 6.** Calculate the half-lives for the  $\text{SO}_2\text{Cl}_2$  reaction in Example 1 and for the  $\text{C}_2\text{H}_4$  reaction in Example 4.

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

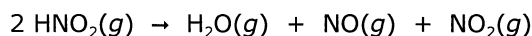
$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693147\dots}{1 \times 2.2 \times 10^{-5} \text{ s}^{-1}} = 32,000 \text{ s}$$

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.

$$t_{1/2} = \frac{1}{ak[A]_0} = \frac{1}{2 \times 0.042 \text{ (L/mol)/min} \times 0.00722 \text{ mol/L}} = 1600 \text{ min}$$

Your turn.

**Example 7.** 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 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 overall. 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  $T$  time.

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

As temperature increases, reactions 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 of those collisions will carry the amount of energy which is needed (or more) in order 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.

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

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 these 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.

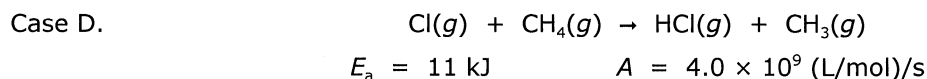
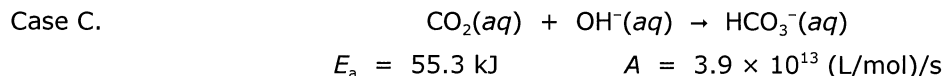
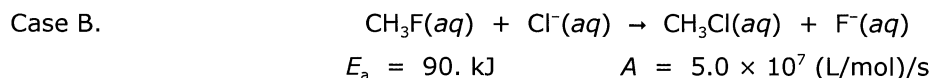
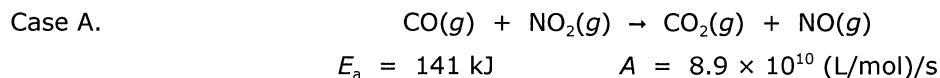
Conceptually, for a reaction with a higher activation energy, the reaction should go slower because fewer collisions will meet the demand of the higher energy barrier. This is reflected in the above equation: the denominator term  $e^{E_a/RT}$  will be larger and  $k$  will therefore be smaller.

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 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.



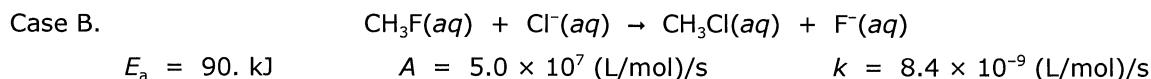
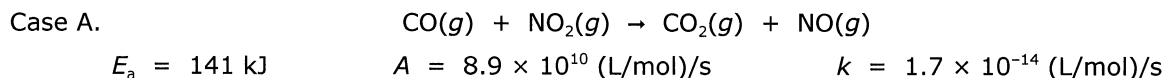
For purposes of calculating  $k$  from  $E_a$  and  $A$  using Arrhenius, you have to be careful with the units in the  $E_a/RT$  part:  $E_a$  is typically in kJ's but  $RT$  gives J's. Here's how that part looks at 25 °C for Case A, after converting  $E_a$  to J's.

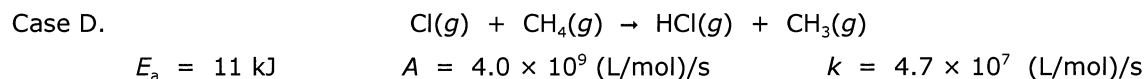
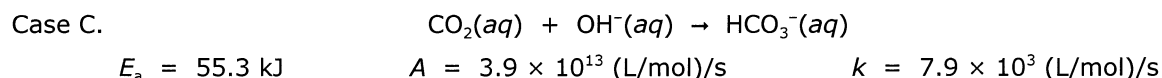
$$\frac{E_a}{RT} = \frac{141,000 \text{ J}}{(8.314 \text{ J/K})(298 \text{ K})} = 56.9105\dots$$

Now take that into Arrhenius.

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

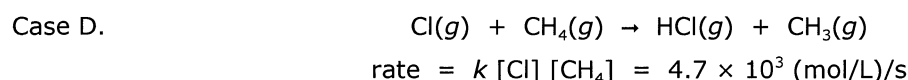
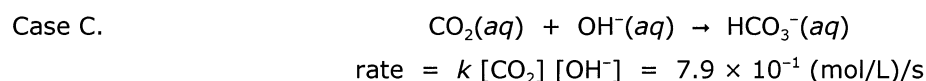
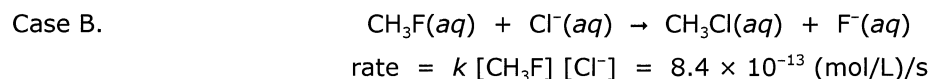
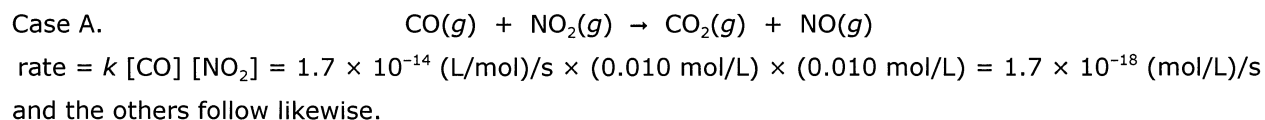
Doing this for each Case above gives the following results (which you should be able to confirm).





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

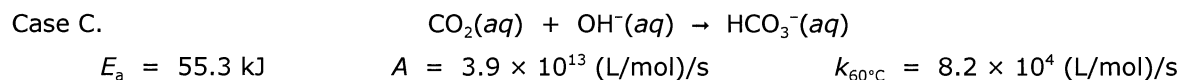
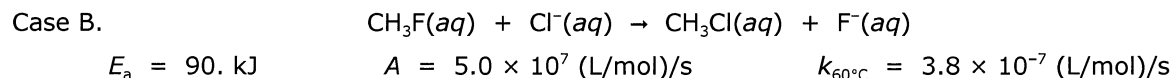


These results span  $10^{21}$  in rates. Case A is basically not happening even though it is exergonic. It would require millions of years. Millions of years are OK in geochemistry but not in the laboratory, so, for all practical purposes, it does not happen. Case B isn't too swift either but it will only take centuries instead of millions of years.

But that's 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.

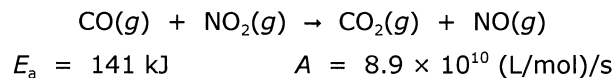


Compare these to the previous values at 25 °C. The  $k$  value for Case B increased 45-fold while the  $k$  value for Case C increased 10.-fold. The different size of the effect is due to the different  $E_a$  values:  $T$  effects are larger when  $E_a$  is larger. For more examples, let's cook up Cases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

**Example 8.** Find the rate constants for Cases A and D at 225 °C.

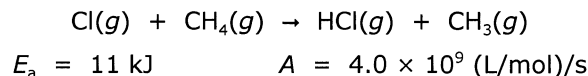
Plug in.

Case A.



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

Case D.



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

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.

The comparison of  $k$ 's at different  $T$ 's for a given reaction can be useful. There is a separate equation which can provide that comparison directly without going through the full Arrhenius calculation twice. The derivation of this equation starts from Arrhenius

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

which is then naturally logged.

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

Set  $k_1$  to be the rate constant at temperature  $T_1$  and  $k_2$  to be the rate constant at  $T_2$ .

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Remember that this is for one specific reaction, so  $E_a$  and  $A$  are the same at both  $T$ 's. Now, subtract these two equations, version 2 minus version 1.

$$\ln k_2 - \ln k_1 = \ln A - \frac{E_a}{RT_2} - \ln A + \frac{E_a}{RT_1}$$

Cancel the  $\ln A$  terms and re-arrange the rest.

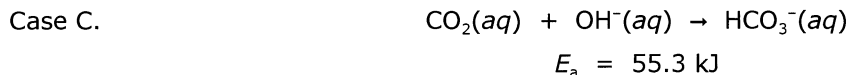
$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

This equation serves several purposes. We can calculate a  $k_2$  at some temperature  $T_2$  if we already know a  $k_1$  at another temperature  $T_1$ . Or, we can calculate a temperature  $T_2$  in order to obtain a rate constant  $k_2$  of some desired value, if we already know the rate constant  $k_1$  at another temperature  $T_1$ . Or, we can use this equation to calculate the ratio of the rate constants  $k_2/k_1$  at different temperatures  $T_1$  and  $T_2$ . We can still do these things with the original version of the Arrhenius equation, but sometimes this version is more handy and it doesn't need the value for  $A$ . Another benefit of this equation is that it allows for the determination of  $E_a$  itself, by measuring rate constants  $k_1$  and  $k_2$  at different temperatures  $T_1$  and  $T_2$ . Finally, this equation confirms that temperature effects are greater when  $E_a$  is greater: for comparing a given  $T_2$  versus  $T_1$ , the effect on  $k_2$  versus  $k_1$  is greater when  $E_a$  is greater.

Although handy at times, this equation is a bit tedious to execute. For one thing, be sure to connect  $k_1$  with  $T_1$  and  $k_2$  with  $T_2$  or you'll mess this up royally. Let's go ahead with an Example.

.....  
**Example 9.** Using Case C: find the ratio of the rate constants at 60. °C relative to 25 °C.  
 .....

We did this upstairs by executing Arrhenius twice, but now we'll do it directly.



Set it up.

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

In this case, we are solving for the ratio itself of  $k_2/k_1$ , with  $T_1 = 25 \text{ °C}$  (298 K) and  $T_2 = 60. \text{ °C}$  (333 K). By the way, you will have an issue with the energy units in  $E_a$  and  $R$ , and they both must be in J's or in kJ's. Here they are in J's.

$$\ln \frac{k_2}{k_1} = -\frac{55,300 \text{ J}}{8.314 \text{ J/K}} \left( \frac{1}{333 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

For sigfig purposes, this is another one of those complicated cases for which strict adherence to sigfig rules is not justified. So, we will simply execute this calculation in its entirety and then round off according to how many sigfigs are provided in the given numbers. The round-off will be to three sigfigs, since there are only three in the  $E_a$  and  $T$  values.

Here's the play-by-play. Do the inverse of each temperature and subtract them.

$$\ln \frac{k_2}{k_1} = -\frac{55,300 \text{ J}}{8.314 \text{ J/K}} (-0.0003527\dots)$$

Finish off the right side. Notice that the two negative signs on the right will cancel.

$$\ln \frac{k_2}{k_1} = 2.3459\dots$$

Take the antiln and you will get a ratio of  $k_2/k_1 = 10.4$ , in agreement with the prior calculations upstairs. The rate is 10.4 times faster at 60. °C compared to 25 °C.

Let's do another variation, now using Case A since it's the slowest.

.....  
**Example 10.** Considering the reaction of Case A, what temperature is needed for the reaction to be 100. times faster than the reaction at 25 °C?  
 .....

This is another ratio question but now you are given the ratio as 100. and you are asked for a temperature. Set up the equation.

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

$k_2/k_1 = 100.$  and  $T_1 = 25 \text{ °C} = 298 \text{ K}$ . Find  $T_2$ .

$$\ln 100. = -\frac{141,000 \text{ J}}{8.314 \text{ J/K}} \left( \frac{1}{T_2} - \frac{1}{298 \text{ K}} \right)$$

Re-arrange.

$$-0.00027154\dots = \frac{1}{T_2} - \frac{1}{298 \text{ K}}$$

$$0.0030841\dots = \frac{1}{T_2}$$

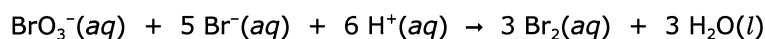
You will get  $T_2 = 324 \text{ K}$  which is 51 °C. That's a small increase in  $T$  for going 100-times faster, but the reaction would still be horrendously slow.

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  $\text{conc}^{-2} \text{ time}^{-1}$ .
  - 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.

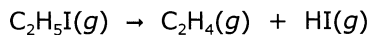
$$\text{rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

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.
- Consider the following balanced equation.
 
$$2 \text{NO}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{ClNO}_2(g)$$
 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.
  - The following reaction is first order in  $\text{C}_2\text{H}_5\text{Cl}$ ;  $k = 4.7 \text{ s}^{-1}$  at 960. K.
 
$$\text{C}_2\text{H}_5\text{Cl}(g) \rightarrow \text{C}_2\text{H}_4(g) + \text{HCl}(g)$$
    - Write the rate equation.
    - What is the rate of the reaction when  $[\text{C}_2\text{H}_5\text{Cl}] = 0.089 \text{ mol/L}$ ?
    - What is the half-life of the reaction?
  - The following reaction is first order in each reactant;  $k = 801 \text{ (L/mol)/s}$  at 298 K.
 
$$\text{H}_2\text{O}(g) + \text{N}_2\text{O}_4(g) \rightarrow \text{HNO}_3(g) + \text{HNO}_2(g)$$
    - Write the rate equation.

b. What is the rate of the reaction when  $[\text{H}_2\text{O}] = 0.116 \text{ mol/L}$  and  $[\text{N}_2\text{O}_4] = 0.0637 \text{ mol/L}$ ?

6. The following reaction is first order in  $\text{C}_2\text{H}_5\text{I}$ ;  $k = 4.0 \times 10^{-3} \text{ s}^{-1}$  at 700 K.



The reaction begins with  $[\text{C}_2\text{H}_5\text{I}] = 3.3 \times 10^{-4} \text{ mol/L}$ . After 100. s,

- what concentration of  $\text{C}_2\text{H}_5\text{I}$  remains?
  - what concentration of HI has formed?
  - what is the percent completion?
7. The following reaction is second order in  $\text{NO}_2$ ;  $k = 0.68 \text{ (L/mol)/s}^{-1}$  at 500 K.



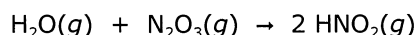
The reactions begins with  $[\text{NO}_2] = 0.0344 \text{ mol/L}$ .

- What is the half-life?
- After 1.0 min,
- what concentration of  $\text{NO}_2$  remains?
  - what concentration of NO has formed?
  - what is the percent completion?
8. The following reaction is first order in  $\text{N}_2\text{O}_5$ ;  $t_{1/2} = 0.29 \text{ s}$  at 325 K.



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

- what concentration of  $\text{N}_2\text{O}_5$  remains?
  - what concentration of  $\text{NO}_2$  has formed?
  - what is the percent completion?
9. For the following reaction,  $E_a = 37.17 \text{ kJ}$  and  $A = 3.78 \times 10^{10} \text{ (L/mol)/s}$ .



What is  $k$  at a temperature of 310. K?

10. Human body temperature is 37 °C, which can give faster reactions than those conducted at 25 °C. Assume a reaction has an activation energy of 63 kJ. What is the ratio of the rate constants for this reaction at these two temperatures? (The requested ratio is for (rate constant at 37 °C)/(rate constant at 25 °C).)