

Chapter 50

DOES IT HAPPEN?

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We are finally arriving at the answer to the question of "Will it happen?" for an exergonic process. The answer is: It depends. Before we go there, let's go backwards.

50.1 Getting into reverse

The emphasis since Chapter 48 has been going forward but, if you're going to be in balance, then you have to be able to look backwards. Recall once again The Big Two from Chapter 35.

“ There are two approaches to describe the balance which is associated with any equilibrium.

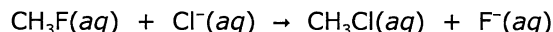
1. The first approach is by the speeds (rates) of the opposing processes. At the point of equilibrium, these speeds are equal and in balance. This approach is the kinetic description of equilibrium.
2. The second approach is by enthalpy and entropy. At the point of equilibrium, a system's enthalpy and its entropy are in balance. This approach is the thermodynamic description of equilibrium. ”

We completed the second of The Big Two in Chapters 45 - 47. Now here in Chapter 50, we complete the first of The Big Two, although we had been dealing with it since the equilibrium of phase changes in Chapter 35. We can now wrap up both of The Big Two and summarize them collectively as follows.

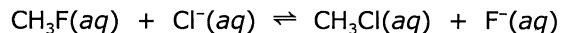
At equilibrium, the forward speed equals the reverse speed.
At equilibrium, $\Delta G = 0$.

Remember these.

We haven't done much yet with the reverse speed in kinetics so we now take some time to elaborate on that direction. We return to the First Example of Chapter 48.



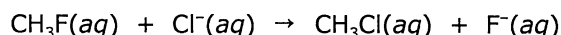
This equation was the single elementary step for the reaction. We now consider this as an equilibrium process.



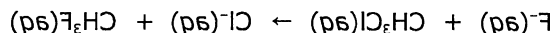
ΔG° for this reaction was given as -2 kJ. From this, you can calculate the equilibrium constant K to be 2. (By the way, don't confuse equilibrium constant K with rate constant k .) The K expression is the following.

$$K = \frac{[\text{CH}_3\text{Cl}][\text{F}^-]}{[\text{CH}_3\text{F}][\text{Cl}^-]}$$

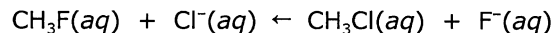
(Also by the way, don't forget that capital K has no units but little k does.) At equilibrium, the forward reaction will be happening



and so will be the backwards or reverse reaction.



Oops.



The rate laws are given by

$$\text{rate}_{\text{fwd}} = k_{\text{fwd}} [\text{CH}_3\text{F}] [\text{Cl}^-]$$

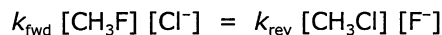
$$\text{rate}_{\text{rev}} = k_{\text{rev}} [\text{CH}_3\text{Cl}] [\text{F}^-]$$

where the subscripts fwd and rev are for the forward and reverse directions. Notice that the reverse rate law was written based on the reverse direction also being an elementary step. This is general: every elementary reaction is elementary in both directions.

At equilibrium balance, the forward speed equals the reverse speed.

$$\text{rate}_{\text{fwd}} = k_{\text{fwd}} [\text{CH}_3\text{F}] [\text{Cl}^-] = \text{rate}_{\text{rev}} = k_{\text{rev}} [\text{CH}_3\text{Cl}] [\text{F}^-]$$

From the equal rates



we can derive

$$\frac{k_{\text{fwd}}}{k_{\text{rev}}} = \frac{[\text{CH}_3\text{Cl}] [\text{F}^-]}{[\text{CH}_3\text{F}] [\text{Cl}^-]}$$

and this is the same as the equilibrium K expression from above.

$$K = \frac{k_{\text{fwd}}}{k_{\text{rev}}}$$

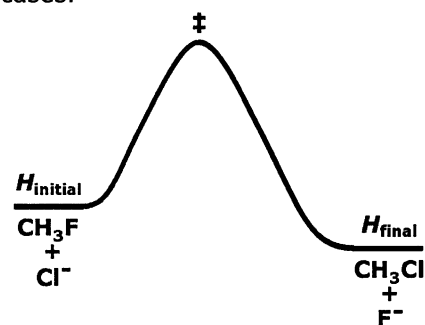
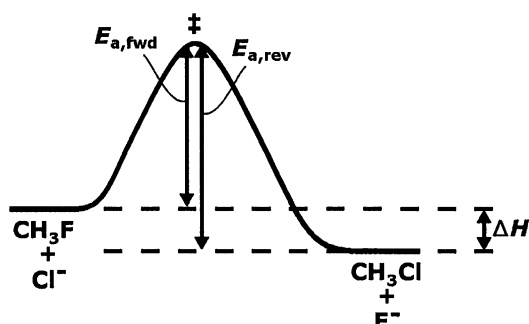
This result applies for elementary reactions: the equilibrium constant K equals the ratio of the rate constants, forward over reverse. This provides a means for calculating a K or a k_{fwd} or a k_{rev} if the other two are known. For example, as determined in Section 49.4 for this reaction, $k = 8.4 \times 10^{-9}$ (L/mol)/s and that was for the forward direction. We can now determine k_{rev} from this and K .

$$k_{\text{rev}} = \frac{k_{\text{fwd}}}{K} = \frac{8.4 \times 10^{-9} \text{ (L/mol)/s}}{2} = 4 \times 10^{-9} \text{ (L/mol)/s}$$

This calculation is straightforward for this case, but complications can arise when the reaction involves a mix of solute and gas components. We'll stick with the simpler cases.

Let's return to the reaction energy diagram and take a look at it in the reverse direction. At right is one of the versions for this reaction from Chapter 48. As given then, $\Delta H = -23$ kJ and $E_a = 90$ kJ for the forward direction. Now we re-examine the R.E.D. in both directions, forward and reverse. This version, directly below, shows $E_{a,\text{fwd}}$ and $E_{a,\text{rev}}$. Notice that the two values differ by ΔH . This is always true and we can write this as follows.

$$\Delta H = E_{a,\text{fwd}} - E_{a,\text{rev}}$$



For the present example, we can re-arrange this equation to find $E_{a,\text{rev}}$.

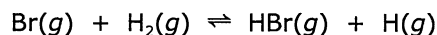
$$E_{a,\text{rev}} = E_{a,\text{fwd}} - \Delta H$$

$$E_{a,\text{rev}} = 90. \text{ kJ} - (-23 \text{ kJ}) = 113 \text{ kJ}$$

The energy barrier to go backwards is greater than to go forward, $E_{a,\text{rev}} > E_{a,\text{fwd}}$. THIS WILL BE TRUE FOR EVERY EXOTHERMIC REACTION.

Let's now take a look at another example.

Consider the following reaction at 500. K. The equation shown is an elementary step.

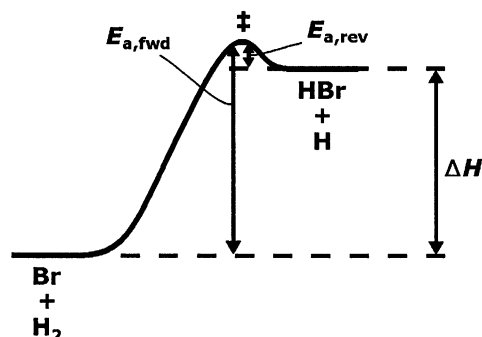


Since elementary, it is elementary in both directions and we can deduce from the balanced equation that the process is second order in the forward direction and second order in the reverse direction.

$$\text{rate}_{\text{fwd}} = k_{\text{fwd}} [\text{Br}] [\text{H}_2]$$

$$\text{rate}_{\text{rev}} = k_{\text{rev}} [\text{HBr}] [\text{H}]$$

For this reaction, $\Delta G^\circ = 65.83$ kJ and this gives an equilibrium constant $K = 1.33 \times 10^{-7}$ at 500. K. The activation energies are $E_{a,\text{fwd}} = 80.2$ kJ and $E_{a,\text{rev}} = 10.1$ kJ and these are depicted in the R.E.D. at right. From these two values, you can calculate $\Delta H = 70.1$ kJ. Here, the energy barrier to go backwards is less than to go forward,



$E_{a,rev} < E_{a,fwd}$. THIS WILL BE TRUE FOR EVERY ENDOTHERMIC REACTION. The rate constants for this system are $k_{fwd} = 720$ (L/mol)/s and $k_{rev} = 5.6 \times 10^9$ (L/mol)/s. At equilibrium, the forward speed will equal the reverse speed

$$k_{fwd} [\text{Br}] [\text{H}_2] = k_{rev} [\text{HBr}] [\text{H}]$$

which re-arranges to

$$\frac{k_{fwd}}{k_{rev}} = \frac{[\text{HBr}] [\text{H}]}{[\text{Br}] [\text{H}_2]}$$

which is again equal to the equilibrium constant for the reaction by a straightforward calculation.

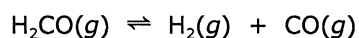
$$\frac{k_{fwd}}{k_{rev}} = \frac{720/\text{s}}{5.6 \times 10^9/\text{s}} = 1.3 \times 10^{-7}$$

While we're here looking at reaction energy diagrams, let's bring in a few more of them and a few more points about them.

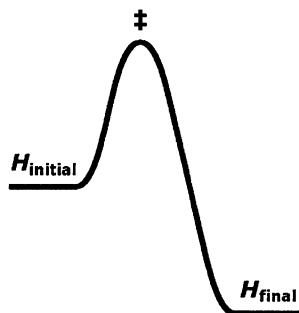
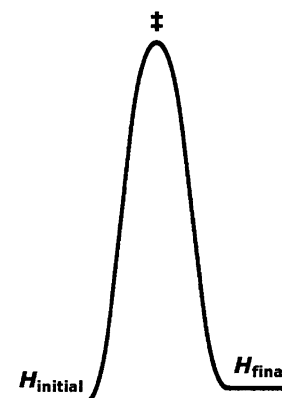
50.2 In the R.E.D.

Reaction Energy Diagrams are useful visual tools for a quick glance at activation energies (both directions) and reaction enthalpies. We've only seen these for two reactions so far and these were for single elementary steps. Here are additional examples for illustration purposes.

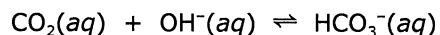
Formaldehyde, H_2CO , reacts at high temperatures in several different ways, one of which is dissociation to form H_2 and CO .



This elementary reaction has a very high E_a of 301 kJ but a small $\Delta H = 12.5$ kJ at 1,400 K. (By the way, if you are given E_a without a label such as $E_{a,fwd}$ or $E_{a,rev}$, then assume it's forward.) The R.E.D. for this reaction is shown at right. This diagram is primarily one big bump with a comparatively small difference between H_{final} and $H_{initial}$. I've left out the arrows and such but feel free to draw them in if you wish. You can also go ahead and calculate the value for $E_{a,rev}$.



Next, consider again the reaction of aqueous CO_2 with OH^- which was Case C in the last Chapter.

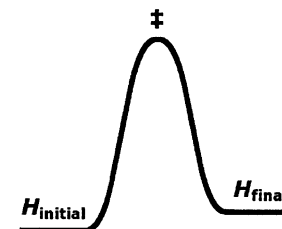


This is a simple reaction with importance to biology, geochemistry and atmospheric chemistry. (Atmospheric chemistry? Aqueous? Yes, many reactions in the atmosphere are in the gas phase but some are aqueous since these occur in liquid water droplets in the air. There's also ice and snow chemistry!) The $E_{a,fwd}$ for this reaction is 55.3 kJ and ΔH is -48.2 kJ. From this you can calculate $E_{a,rev}$. The R.E.D. is shown at left.

For a medical application, consider cisplatin which has been a very important anti-cancer drug for decades. Its formula is $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Inside a cell, it reacts slowly with water.



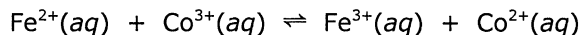
This reaction has $E_{a,fwd} = 85$ kJ and $E_{a,rev} = 77$ kJ, from which you can calculate ΔH which will tell you the reaction is endothermic. Or you can see that it is endothermic in the R.E.D. at right.



These are just additional illustrations of the various shapes which a reaction energy diagram can take. You should be able to draw such a diagram and, in order to be able to do that, you need ΔH and at least one of $E_{a,fwd}$ or $E_{a,rev}$. Or, if you're given $E_{a,fwd}$ or $E_{a,rev}$ without ΔH , then you need to get ΔH from those.

$$\Delta H = E_{a,\text{fwd}} - E_{a,\text{rev}}$$

In setting up the R.E.D., the sign of ΔH is as important as the number itself. Keep that in mind as we illustrate the process by drawing the R.E.D. for the following reaction. This is a simple aqueous redox reaction.



This reaction has $\Delta H = -110. \text{ kJ}$ and $E_a = 41 \text{ kJ}$.

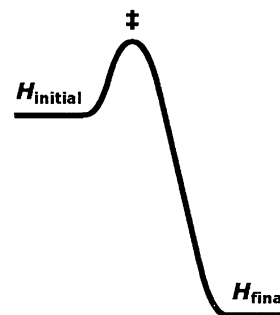
To start the R.E.D., begin with a first line on the left side somewhere for your initial enthalpy. Then, draw a second line at the right side for your final enthalpy. This is where you need to know whether the reaction is exo- or endothermic. For an exothermic reaction, the right line is lower than the left line because the system ends at lower energy. For an endothermic reaction, the right line is higher than the left line because the system ends at higher energy. The given reaction is exothermic, so draw the right line lower than the left. How far down should the right line be? If you're drawing this to some scale, then use whatever scale. Otherwise, just eyeball something that looks good. $110. \text{ kJ}$ is sizeable, so draw something lower by a sizeable amount, as shown at right.



Somewhere between the left and right lines and somewhere high, you will need to indicate the transition state energy. How high? Again, if you're drawing this to scale, then use whatever scale. Otherwise, eyeball something which reflects the spacing for your ΔH . The ΔH is $-110. \text{ kJ}$ and the E_a is 41 kJ , so the E_a space is a bit more than a third of the ΔH space. Place a dot thereabouts on the R.E.D. as shown at left.

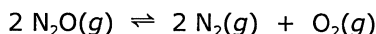


Now connect the left line to the dot with a curve and keep drawing past that down to the right line. Voila! Fill in your labels if you want to. Your finished artwork appears at right. You can put in the E_a 's if you want.



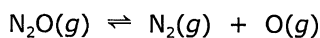
OK, all of the R.E.D.'s so far have been for single steps. Let's complicate this a bit and bring in an R.E.D. for a composite process. We won't do four steps as done for the Second Example in Chapter 48; we'll just do a two-step.

Dinitrogen oxide, N_2O , is a strong oxidizing agent but it typically has large activation energies toward reacting. Thus, it doesn't react much at room temperatures. That's why they can use it as a mild anesthetic and as a propellant in cans of whipped cream. It's "laughing gas". Start cooking it to high temperatures, however, and it can get very reactive, especially towards fuels. In fact, it has been used in cars and other vehicle engines for extra power. (In that application, it's known as "nitrous" which derives from its older name of nitrous oxide.) By itself at high temperatures, N_2O can react to form its elements.



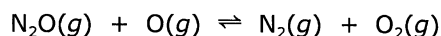
This is a composite reaction comprised of two elementary steps.

Step 1.



$$\Delta H_1^\circ = 168.7 \text{ kJ} \quad E_{a1} = 241 \text{ kJ}$$

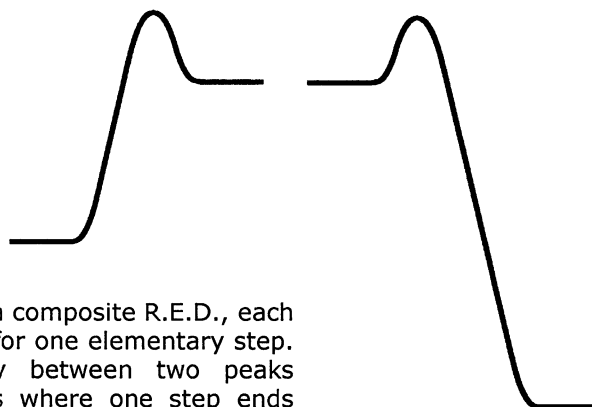
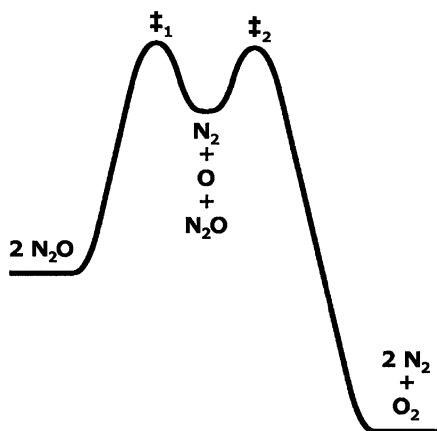
Step 2.



$$\Delta H_2^\circ = -337.7 \text{ kJ} \quad E_{a2} = 67 \text{ kJ}$$

The values shown are for $1,200 \text{ K}$. You can sum these two equations and you will get the overall equation for which $\Delta H^\circ = -169.0 \text{ kJ}$. In this mechanism, the O atoms are intermediates.

The R.E.D. of a composite mechanism is composed of the R.E.D.'s of the individual steps. At right are the separate R.E.D.'s for Steps 1 and 2. To get the overall R.E.D., you simply connect them such that Step 2 picks up where Step 1 left off. This is shown directly below with the ingredients labeled.



In a composite R.E.D., each peak is for one elementary step. A valley between two peaks indicates where one step ends and the next step begins. This valley also indicates the energy of the system at which intermediates are present along with other reactants and products, if there are any. The reactants of the overall equation are shown at far left and the products of the overall equation are shown at far right. In the first step, one N_2O reacts to produce one N_2 and one O , and these are shown in the middle (along with the second N_2O which hasn't reacted yet). We can see from this R.E.D. that the process has a very large E_{a1} . Once reaching that first peak, some energy can be released heading down to the intermediate valley but then a

second energy barrier is encountered as E_{a2} . After that, however, it's all downhill to reach the final product state. Since E_{a1} is so much larger than E_{a2} , the first step is the killer in terms of how fast the overall reaction will actually run. This is a case where one step is much slower than the other and this slow step is then the rate determining step.

The two peaks in this composite R.E.D. may look to be at the same level but they are a tad different. Composite R.E.D.'s for other reactions and mechanisms usually have peaks at very different levels and it will just depend on the circumstances.

OK, enough artwork. Now it's time to really speed things up.

50.3 Catalyst for change

As we have seen, for a given reaction with a given mechanism, there is some value of E_a and some value of A . These and a value for T will give the rate constant k . This k and the concentrations will give the speed for the reaction. You can vary T and/or concentrations to allow some variations in speed but wide variations are frequently not possible. Thus, there may be limitations on how fast a given reaction can go with a specific mechanism. That's not necessarily the end of the story, however, and often there is another option.

Change the mechanism.

Changing the mechanism gives a different E_a and A . E_a has the bigger effect on k so, for a faster reaction, you primarily want a mechanism with a lower E_a . OK, fine. How do we do that?

Bring in a catalyst.

A catalyst is a component in the system which speeds up the overall reaction by reacting or interacting with a reactant or with an intermediate. This reaction/interaction constitutes a new and different step and this means it's a different mechanism. The chemical identity of the catalyst changes during one step of the process but it changes back to its original identity in a later step. In other words, the catalyst starts and ends the overall process as the same chemical species, but it changes to and fro in the middle. The balanced equation for the overall reaction stays the same and only the mechanism is different. Some catalysts make some processes go a little faster and some catalysts make some processes go billions of times (or more) faster. It depends on the process and it depends on the catalyst.

Here's a bit of terminology. The catalyst is the agent which speeds up the overall reaction. The verb is catalyze. The noun catalysis refers to the general field of study of catalysts or to the use of a catalyst in some process.

Catalysts play key roles in all sorts of things, good and bad. They are a major part of the natural world and they are a major part of the industrial world. Human society could not function without them. Their uses range in scope from the largest industrial processes on the planet down to an individual consumer driving around with one on the underbelly of their fossil-fuel-driven car. Even the human body could not function without catalysts. In fact, every cell of all life on Earth requires them.

For an illustration of a catalyst, let's take a look at ozone, O_3 . Ozone is friend and foe. It is friend to all surface critters on Earth because it exists in the upper atmosphere (stratosphere) where it absorbs much of the UV light from the Sun. Although numerous substances in the atmosphere absorb UV light, O_3 absorbs up to the 310 nm range and is better than the others for that range. If surface Earth received a bigger blast of that UV radiation from the Sun, direct sunlight would be far more dangerous to organisms, including humans. Although of life-saving benefit in the stratosphere, ozone at Earth's surface is a foe because it is quite reactive and it causes degradation of many kinds of materials including biological tissue (such as your respiratory tract), and that adversely impacts health.

For our illustration here, we will consider several elementary steps which are involved in forming and reacting with ozone in the stratosphere. The Steps are labeled A - D here and not numerically because they do not necessarily happen in the sequence which is given.



This is a photochemical step which requires a UV photon of ~ 240 nm or shorter wavelength. This is a high energy photon and that high energy is needed to break the very strong $O=O$ double bond.



This Step has no energy barrier.

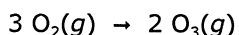


This Step has a small E_a of 17 kJ.

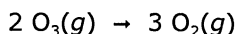


This Step is another photochemical Step and it requires UV photons of ~ 310 nm or shorter wavelength in order to break apart an ozone molecule.

Steps A and B are the Steps which together produce O_3 while each of Steps C and D react it away. These four Steps are not happening to the same extent, so we cannot take a simple sum of the equations. The net outcome, however, is the formation of O_3 from O_2



and the decomposition of O_3 back to O_2 .



This leaves some concentration of O_3 present at all times depending on light level, temperature, mixing of air, other substances present, etc.

Notice "other substances present".

Humans have been putting "other substances" into the atmosphere for many years, and some of those are eventually ending up in the stratosphere and messing with the ozone layer. The reason for them messing with the ozone layer is that these other substances catalyze the decomposition of ozone and therefore reduce the concentrations which are naturally present. One example of such a catalyst is atomic chlorine.

As noted in the Second Example of Section 48.2, Cl atoms are very reactive radicals. They are present in the upper atmosphere at minute levels. Some of that arises from natural sources but much arises from human sources, in large part from the manufacture and use of chlorofluorocarbons over many years. Chlorofluorocarbons are compounds of Cl, F and C, and sometimes H. These were in very widespread use as refrigerants, blowing agents, propellants and other applications for decades. These were first mentioned back in Chapter 5, as was also their notoriety.

“ Many of these compounds had been used for refrigeration (and for various sorts of other things, too) for years, but the ones containing chlorine were getting into the upper atmosphere and destroying the ozone layer. (We'll discuss some of this later in Chapter 50.) ”

Later is now. As a whole, these compounds are fairly unreactive which rendered them fairly safe, but that also allows them to migrate upwards into the stratosphere; there, under intense solar exposure, they react to produce monatomic Cl. Those are the major culprits. The increase in Cl from human sources is a major contributor to the decline in ozone levels in the upper atmosphere, although these practices have been curtailed to substantial extent in recent decades.

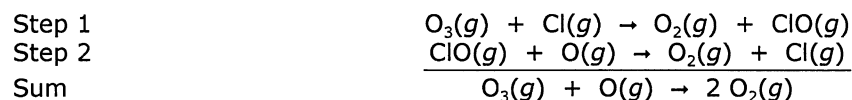
Cl atoms catalyze the breakdown of ozone by a two step process as illustrated by the following sequence. These are elementary steps.



This is a direct take-down of an ozone molecule by an atom of Cl. The E_a is 2 kJ, which means easy. If this were the end of the story, it wouldn't be so bad. But it's not the end of the story.



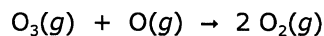
The ClO from Step 1 reacts to form Cl which then goes back into Step 1 to take down another molecule of ozone. This Step 2 has no energy barrier. These two Steps constitute a chain and they can cycle over and over again, taking down more and more ozone each time. The net outcome is the sum of the two Steps.



This Sum is the same as single Step C upstairs. Thus, the reaction of $\text{O}_3 + \text{O}$ is now operating directly via Step C and also catalytically via Steps 1 and 2, so the loss of ozone is accelerated. Note that the Cl catalyst reacts in Step 1 but is formed again in Step 2. In the summation overall, the catalyst drops out of the equation. Note also in this scheme that ClO is an intermediate; it is formed in Step 1 but reacts in Step 2 and it, too, drops out of the overall equation. By the way, don't confuse a catalyst and an intermediate. Both drop out for the overall equation but their sequence of action is different. A catalyst reacts in one step and is formed back in a later step. An intermediate is first formed in one step and then reacts in a later step. The sequences are subtly different but it's an important difference.

Comparing activation energies, single Step C has $E_a = 17$ kJ while Step 1 has $E_a = 2$ kJ and Step 2 has no energy barrier. Thus, the catalyzed steps have lower E_a and are potentially much faster, although speed also depends on concentrations. Since ozone elimination is accelerated by the catalyzed Steps 1 + 2, the concentration of O_3 which is present in the stratosphere is now lower. By the way, original Steps A - D are still operating although their speeds may be affected by the changes in concentrations brought about by the catalysis.

Since the overall equation for the catalysis (Sum of Steps 1 + 2) is the same as the original Step C equation, then the thermodynamic parameters (ΔH° , ΔS° and ΔG°) are not changed. The reaction



has the same thermodynamic parameters of ΔH° , ΔS° and ΔG° whether it is catalyzed or not. This is also an important point to note.

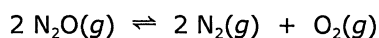
This example highlights the general features of catalysts. Let's summarize.

- Catalysts speed up a reaction by operating in a different mechanism. This new pathway serves in addition to the original pathway of the uncatalyzed reaction. Although the uncatalyzed reaction can still operate, it may no longer be significant if the catalytic reaction is much faster (say, 100-fold faster or more).
- During each run of the overall process, the catalyst reacts in one step but is formed back again in a later step. Since at least two steps are involved, then catalyzed mechanisms are composite mechanisms.
- Once returned to its original identity, the catalyst can catalyze another round of reaction(s). This can go on and on and on, and one molecule of catalyst may affect hundreds or thousands or more molecules of reactant or of intermediate. For this reason, catalysts are commonly present in small amounts relative to the amount of reactants present.

- The catalyst does not change the initial state (reactants) or the final state (products) of the overall reaction. Thus, it does not change the thermodynamic parameters (ΔH° , ΔS° , ΔG° and K) for the overall process. On the other hand, the catalyzed mechanism does provide different kinetic parameters of E_a , A and k .

By the way, since a catalyst speeds up a reaction by providing steps with lower E_a 's, then both the forward and the reverse speeds are impacted. Thus, a catalyst speeds up a reaction in both directions. All of these aspects are important for all catalysts.

Of the many different catalysts known in many different applications, there are two broad categories: homogeneous and heterogeneous. These terms carry the same meaning here as they do for mixtures in general. In the ozone example above, everything was in gas phase including the catalyst itself; as such, Cl is a homogeneous catalyst. For solution reactions, if the catalyst is dissolved with everything else, then it is again homogeneous. There are many catalysts that operate as solids, however, even though the reaction may be gas phase or solution phase. Those catalysts are heterogeneous. Solid catalysts operate by their surfaces, which can include outside and inside surfaces. Many solid catalysts have channels which penetrate into the solid and thus provide more surface area along those channels. Reactants and or intermediates bind to atoms on the surfaces of the solid and this leads to the catalytic activity. For example, the prior reaction of N_2O ,



with its foreboding first step E_a of 241 kJ, is catalyzed by several different metals using different elementary steps. Catalysis by platinum results in an E_a of only 134 kJ while gold does better at 121 kJ. These are huge reductions in the energy barrier.

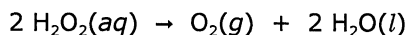
Let's consider a commonplace example of catalysis which applies to something which many people have in their home: hydrogen peroxide. H_2O_2 is typically found in stores as an aqueous solution at 3% concentration for use as a mild antiseptic. There are three things to note when you buy this product.

The bottle is brown.

The bottle is plastic.

Somewhere on the label, it probably says "stabilized".

The first is about light. The second is about catalysis. The third is about the opposite of catalysis. They're all about what H_2O_2 would like to do exergonically, and that is to decompose to O_2 and H_2O .



At standard conditions, $\Delta G^\circ = -206.22$ kJ and that is a substantial driving force, but the reaction is slow at room temperature due to a step with a considerable E_a of ~ 70 kJ. Thus, the decomposition should be slow and the product should have a reasonable shelf life, but it doesn't necessarily work that way. H_2O_2 is a great example for kinetics because so many different things can affect the rate of its decomposition reaction.

Although the thermal mechanism may be slow, there is also a photochemical mechanism. That means the solution of H_2O_2 is light sensitive. That's why it's sold in brown bottles to block the light.

Even without light, the thermal decomposition of H_2O_2 is unusually sensitive to a wide variety of homogeneous and heterogeneous catalysts, even when those catalysts are present as accidental impurities at very low levels. For example, $Fe^{2+}(aq)$ catalyzes the overall reaction by a mechanism with a 42 kJ barrier, and it is important to avoid such impurities. Glass will also catalyze the reaction. Glass is a solid mixture of various components in its bulk and on its surface. Some components of glass can leach into the solution over time and catalyze the reaction homogeneously. The glass surface can also catalyze the reaction heterogeneously and even microparticles of glass can do this. Because glass is a catalyst for decomposition, H_2O_2 is sold and stored in plastic bottles. Although not a practical concern for the common commercial product, there are other examples of catalysis for the decomposition of H_2O_2 . For example, $I^-(aq)$ catalyzes the reaction via a mechanism with only 57 kJ as the highest energy barrier, and a colloidal dispersion of Pt metal can do this for 50 kJ.

To further slow down the decomposition reaction in commercial solutions of H_2O_2 , a stabilizer is typically added. A stabilizer is some agent whose purpose is to stabilize something from doing an undesirable reaction. It can do this in various ways such as react with some intermediate in the overall process or react with an impurity which would otherwise catalyze the decomposition. In other words, its job is to slow down a reaction. As such, its work is opposite that of a catalyst. A stabilizer is sometimes called an inhibitor, since it inhibits an unwanted reaction.

All of these aspects of kinetics are involved in a simple bottle of H_2O_2 . Even with all of these things, however, the decomposition will happen but it happens more slowly. So that old bottle of H_2O_2 in your medicine chest may not be any good anymore. Check the date on the bottle.

Let's up the scale on the examples.

On a huge scale, the energy industry uses catalysts extensively for processing crude fuels for energy use and for producing raw materials which are used to make a large number of products for modern society. Some of the earliest steps in the process require catalysts. Due to the enormity of scale of the energy industry, these processes are the largest industrial throughput processes on Earth.

Even outside the energy industry, catalysts are required to synthesize some of the largest volume chemical compounds. Sulfuric acid is the single, most produced chemical substance, by mass, on a global basis. Why is H_2SO_4 so important? It's the cheapest strong acid to make and its uses are extensive. Its primary use is making H_3PO_4 which is then used to make phosphate fertilizers for agriculture, but H_2SO_4 also has a host of other uses. Sulfuric acid is produced by first burning elemental sulfur to SO_2 . This is easy and exergonic. SO_2 is then oxidized to SO_3 , which is also an exergonic reaction but very slow, and this part requires a heterogeneous catalyst. Ultimately, SO_3 and H_2O are combined, albeit indirectly, to make H_2SO_4 . (These are industrial stages and not elementary steps.) Interestingly, although H_2SO_4 is the most synthesized compound by mass, ammonia is the most synthesized by moles: there are more moles of NH_3 produced than any other single compound. NH_3 is produced catalytically using N_2 from the air and H_2 which is produced from fossil fuels. The primary uses of NH_3 are also in fertilizer production for agriculture: NH_3 is used directly and it is used to make other fertilizers. As you can see, these chemical processes are hugely important to agriculture. Fertilizers increase crop production. Crops can be eaten directly by humans and crops are also used to feed animals which are eaten by humans. In the case of ammonia, for example, it has been estimated that ~30% or more of the Earth's population would not exist without industrial NH_3 production. That's a positive. But the process consumes massive quantities of H_2 and the synthesis of H_2 on that scale releases massive quantities of CO_2 . That's a negative. Furthermore, there are serious health and environmental issues with the ammonia itself. Fertilizer runoff from farmlands causes ecological problems downstream. And, the escape of NH_3 to the air contributes to the formation of air-borne particulate matter, which is an especially harmful form of pollution. More negatives. These points serve to illustrate the complexity of issues which face modern society.

Let's get back to your underbelly.

Vehicles powered by fossil fuels carry catalytic converters in order to clean up the exhaust from the engine. The converter is commonly located on the vehicle's underside in the exhaust line, somewhere between the engine and the muffler. Fossil fuels are primarily hydrocarbons. The main engine output is CO_2 and H_2O but exhaust also contains quite a bit of other things as it leaves the engine. The concentrations of those components need to be reduced before release to the atmosphere. The biggest culprits are CO, nitrogen oxides and remnants of fuel molecules which were not fully combusted. (The nitrogen for the nitrogen oxides come from N_2 of the air.) These things are unhealthy directly and/or they contribute to acid rain and to smog which are also unhealthy. The job of the converter is to catalytically react the CO and fuel fragments to CO_2 and H_2O , and to react the nitrogen oxides back to N_2 , all before they exit the tailpipe into the environment. Unfortunately, CO_2 emissions are also harmful in the long term but that's a separate issue of very major concern.

Biologically, many cellular reactions are catalyzed. Most biological catalysts are protein-based enzymes and all life on Earth depends on the many different enzymes in their systems. The chemical units are monstrous structures in the tens-of-thousands of g/mol range, with some even more massive at over 500,000 g/mol. Enzymes are among the fastest, finest, best-tuned catalysts known. Some biological reactions which would take millions of years to occur without a catalyst can occur in a fraction of a second with the right enzyme. The acceleration of reactions by enzymes can reach up to 10^{19} -fold, which is utterly phenomenal. Enzymes have to be fast, given that their concentrations in cells are commonly on the order of 10^{-5} M and that life cannot wait for slow reactions. The loss of activity by only one type of enzyme in a human can be fatal.

You just can't live without kinetics and catalysis.

50.4 Some perspective

So where are we in the quest to answer the question, "Will it happen?"

We certainly have covered a few new things in this and the past two Chapters. The study of kinetics involves looking at reactions in a different kind of way because we are now looking at how they actually

work and not just the overall process. Kinetics deals with all sorts of strange chemical oddities, including many radical characters. Besides the usual reactants and products, there are transition states to consider and maybe some intermediates also in there somewhere. There's an energy barrier to worry about which is totally separate from the usual ΔH of the reaction. Even the direction of collision is important. And then there's time.

Time is a very practical matter. A timeframe of ten minutes for a reaction in the laboratory is very convenient; a timeframe of ten days is much less so, and a timeframe of ten weeks is worse. Heating can speed up a process, but it depends on how much faster it goes for how much hotter. In industry, time and temperature are money, often on a huge scale, and rates become an important consideration. Ironically, it is also possible that reactions can go too fast, in which case we can slow them down by cooling. It may seem odd for a reaction to be too fast but it often happens that, if things are too reactive, then they can do additional reactions than just the one that you want, and that can decrease your yield. In those cases, cooling helps to slow things down and control the vigor.

The time for the reaction to take is inversely connected to the speed of the reaction: a faster reaction takes less time. The rate law provides an arithmetic relationship for the speed based on the rate constant, k , and the concentrations of one or more components. Concentrations can be changed, and increasing the concentration of one or more of the components in the rate law will speed up the reaction.

The rate constant k is connected to the pre-exponential factor, A , and the activation energy, E_a , and both of these are determined by the specific mechanism involved. We cannot change these unless we change the mechanism itself. On the other hand, k is also connected to T and we can change that. E_a is a large part of k and a large part of whether an exergonic reaction will actually happen in a given period of time. The thermal energy contained within the system is typically the source of the energy needed for one or more molecules to form the transition state and to surmount the energy barrier. That connection to T allows us to speed things up by heating the system. We can also speed things up by calling on a catalyst to change the mechanism itself, thus changing E_a and A , but catalysts aren't available for every reaction, so that is often not an option. Although we haven't done much with photochemical reactions, these derive their energies from photons and, for these cases, more intense (brighter) lights will speed up the reaction.

Kinetics is not just an interest in the laboratory or in industry. It's part of you and part of your life. For example, consider the simple need for an ignition source for burning fuels and such. Combustions involve composite mechanisms with lots of radical intermediates. A typical combustion requires a spark or small flame in order for the fuel to start burning with the O_2 of the air. The first step in a typical fuel/ O_2 reaction has a large E_a in the range of 200 kJ or more. Thus, the reaction will not start (or is too slow) at room temperature even though the overall combustion is exergonic with a very large driving force. A spark is needed to get some of the sample's molecules up and over that first large energy barrier and to generate radicals for the various steps involved. It doesn't even have to take much of a spark, and a small discharge of static electricity can serve the purpose. Some applications, such as self-contained explosives and rocket engines, contain their own fuel/oxidizer mixture and don't need O_2 , but even these typically still need a trigger. In some applications, mechanical triggers are used instead of sparks and the mechanical impact provides the energy for initiation. All of these applications are characterized by a large E_a in an early step; once overcome by some molecules, then they release energy to get other molecules going, etc. etc. etc. On the other hand, there are some things that will start their own fires without needing a trigger of any kind. Pyrophoric materials will do this; they will simply catch on fire when exposed to air without any kind of trigger. Why? These have a small E_a for reacting with O_2 so they will start their burn by themselves with just the thermal energies of ordinary temperatures.

You should go back and read the first point at the end of Section 6.2.

Speaking of combustion, the history of kinetics has involved a very large focus on high temperature processes, and rates have been measured in the gas phase for many reactions at hundreds and thousands of kelvins. Some of these reactions and their conditions may seem strange, but these processes lie at the heart of the globally humongous combustion energy industry, along with applications in propellants and explosives. An understanding of mechanisms and rates helps to increase the efficiency of the process.

In addition to the many applications to human society, rates and mechanisms for natural processes also receive intense interest. All of life involves a balance of speeds of reactions acting in concert. Cellular reactions must occur within a reasonable range of speeds, or disease and death can result. The atmosphere of Earth is another example of keen kinetic interest. Air is an incredible soup of tremendous numbers of the good, the bad and the ugly. Beyond the major components of N_2 , O_2 , Ar, and H_2O , there

are many other elements and compounds including free radical intermediates, such as the ubiquitous OH, which are present at ppm, ppb and even lesser amounts. Many of these participate in atmospheric chemistry to some extent, whether it be the chemistry of clean air or the chemistry of polluted air. Furthermore, the atmosphere during daylight is bathed in a frenzied fury of photons of varying energies from the Sun, and these cause photochemical reactions to occur within the air. As such, the chemistry of the atmosphere differs between night and day. It also varies with the seasons and it varies with the altitude. The oceans are also awash in chemistry, as also is the landscape but on a totally different timeframe. All of these processes are ongoing, some in balance and some not in balance, and their condition at any point in time depends on the various rates of the various reactions which are occurring. The interests don't stop on Earth. Astrochemistry deals with the ultra-cold and the ultra-hot, as well as ultra-low concentrations in the interstellar medium in such incredibly small numbers as 0.000000000000000001 mol/L. At these concentrations, collisions between any two particles become rare events. One collision of two atoms/molecules/ions may take months or years, compared to nanoseconds in the atmosphere at Earth's surface. Trimolecular collisions are not realistic at these low concentrations and, essentially, trimolecular steps cannot even occur.

These things are part of your world, and of your universe.

Now, the wrap up.

50.5 Another path completed

From the opener to Chapter 44:

“ But enthalpy and entropy assume pre-eminent roles in all things that happen, not just phases. We shall see their impact on all things as we go through this and many later Chapters. Along the way, we consider two fundamentally important questions related to anything you ever do, to any reaction ever run, or to any process whatsoever. Those two questions are the following.

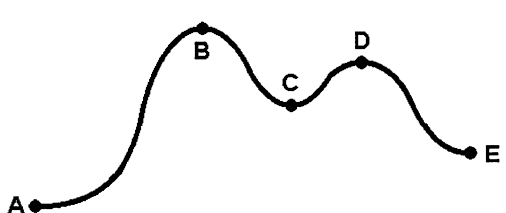
1. Can the reaction or process happen?
2. If it can happen, then will it actually happen?

Can happen and will happen are different. Can happen relates to capability; will happen relates to actuality. ”

We conclude this path of seven chapters, now able to answer these questions. Can happen requires that the process increases the spread of energy across more options; this is reflected in an increase in S_{univ} which is itself reflected in a negative ΔG . This is a thermodynamic consideration. Will happen depends on whether a mechanism makes it feasible within some desired timeframe. This is a kinetic consideration. If both say yes, then it does happen. Otherwise, by itself, it's a no go.

Problems

1. True or false.
 - a. For every exothermic elementary step, $E_{a,\text{fwd}} > E_{a,\text{rev}}$.
 - b. For any reaction at equilibrium, $E_{a,\text{fwd}} = E_{a,\text{rev}}$.
 - c. In every multi-step mechanism, the first step is rate-determining.
 - d. A catalyst lowers the ΔH for the overall reaction.
 - e. Sulfuric acid is the most produced chemical worldwide, based on mass.
2. True or false.
 - a. Reverse activation energies are always greater than forward activation energies.
 - b. At equilibrium, the forward and reverse rates of a reaction are equal.
 - c. On a Reaction Energy Diagram, the maximum on the energy curve for any particular step corresponds to the transition state energy for that step.
 - d. Intermediates and catalysts do not appear in the overall balanced equation for a multistep process.

- e. A catalyst speeds up both the forward and the reverse directions.
3. The following is an elementary step.
- $$\text{NO}(g) + \text{ClNO}_2(g) \rightarrow \text{ClNO}(g) + \text{NO}_2(g)$$
- Write the reverse rate law.
 - List any free radicals which are present (on either side of the equation).
 - Will increasing the temperature increase the rate(s) in the forward, reverse, both or neither directions?
4. Draw a reaction energy diagram for a single elementary step with $\Delta H = -50. \text{ kJ}$ and $E_a = 40. \text{ kJ}$.
5. For the reaction energy diagram at right, answer the following.
- Which point represents the transition state energy of the second step?
 - What two points determine the $E_{a,\text{rev}}$ of the first step?
 - What two points determine the $E_{a,\text{fwd}}$ of the second step?
 - Is the first step exothermic or endothermic?
 - Is the overall process exothermic or endothermic?
- 
6. A reaction has an overall $\Delta H_{\text{rxn}} = -200. \text{ kJ}$. This reaction has two elementary steps. The first step has $\Delta H_1 = -40. \text{ kJ}$ and forward $E_{a1} = 80. \text{ kJ}$. The second step has forward $E_{a2} = 60. \text{ kJ}$. What is the reverse E_{a2} for this second step (in kJ)?
7. A mixture of $\text{H}_2(g)$ and $\text{O}_2(g)$ is explosively exergonic but it may not react at all. Why?