Chapter 48 WILL IT HAPPEN? Part 1

Now that we can tell whether something can happen, we turn to whether it will happen. In order for an allowed reaction to actually happen, there must be some physical means for it to do so. But even when there is some way for it to happen, things can still take time.

48.1 Kinetics

Inherent to the question, "Will it happen?", there is a time component. After you mix all the reactants together and sit there staring at it for several minutes, does the reaction actually happen? Well, there are some reactions that will happen in several minutes but many do not, even though the reaction is exergonic. If it does not happen in several minutes, does that mean the reaction will not happen at all? What if you give it more time? How about after several hours? Does the reaction happen in that timeframe? If not, how about after one day? Still not enough? How about one week? One month? One year? One score? One century? One millennium? Ever? Never?

Thus, the question, "Will it happen?", takes on a sense of time and this gets us into the notion of how fast a reaction occurs. Some reactions can occur in nanoseconds while other reactions may take many years. The notion of how fast a reaction occurs relates to the speed of a reaction, typically called the rate of a reaction.

The study of the speed of reactions is contained within the broader field of chemical kinetics. Chemical kinetics actually addresses two fundamental questions for reactions: "How?" and "How fast?". We've just touched on the latter. "How?" refers to the physical means by which reactant molecules or ions actually produce product molecules or ions. Some reactions occur when a molecule breaks apart somehow. Some reactions occur when two molecules collide with each other. Some reactions involve many steps in the transformation of reactant to product. These things can also be affected by whether the reaction is in the gas phase or solution phase or solid phase or some combination of phases. Together, all of these aspects involve the physical mechanics of chemical change at the molecular level. These details are referred to as the mechanism of a reaction. Thus, "How?" and "How fast?" are contained within the mechanisms and the rates of reactions, and together these make up the study of kinetics. Mechanisms and rates are inherently connected. Ultimately, it is the mechanism which determines the rate but mechanisms cannot usually be determined directly by experiment. On the other hand, rates can be measured experimentally and these measurements are used to support our understanding of the mechanism.

Before jumping in, let me point out that the fields of kinetics and thermodynamics have some overlap but they evolved over the years somewhat separately. Thus, there will be some differences in approach, and I will point out some of this as we go along.

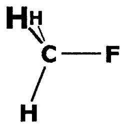
48.2 Two Examples

We'll start with some aspects related to mechanisms. There are many different kinds of mechanisms for reactions and it depends on who's reacting with whom. The various factors which are involved include the atoms present in the chemical unit; the shape of the unit; the presence of electrons in σ or π orbitals and whether such orbitals are bonding, antibonding or lone pairs; the presence of unpaired electrons; etc. The factors can also include the conditions such as phase and even light. We won't be getting into all of these factors because there are too many. For now, we look at two Examples of mechanisms in order to introduce some basic concepts.

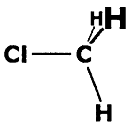
- FIRST EXAMPLE

We start with the reaction in water between CH_3F and Cl^- to produce CH_3Cl and F^-.

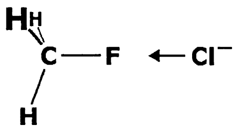
$$CH_3F(aq) + Cl^-(aq) \rightarrow CH_3Cl(aq) + F^-(aq)$$



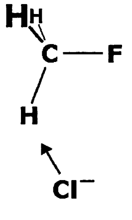
CH_3F goes by the names fluoromethane or methyl fluoride; likewise, CH_3Cl is called chloromethane or methyl chloride. Both of these are covalent compounds. Both are tetrahedral molecules with sp^3 C atoms, as shown at left and right. Both of these compounds are only slightly soluble in water, but they are soluble enough for the reaction to occur. The chloride and fluoride ions for the reaction would be present as some dissolved salt, such as NaCl or NaF. This reaction has $\Delta G° = -2$ kJ, so it is exergonic and allowed at standard conditions but only modestly so. Now, let's take a look at the changes in the chemical units as the reaction proceeds.



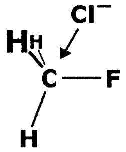
In order for the reaction to occur, a Cl^- ion and a CH_3F molecule must collide. Collisions are a very important part of kinetics and most reactions will involve some kind of collision. Mere collision, however, is usually not enough. Typically, in order for the collision to lead to product, the collision must be hard enough and in the correct direction. These are two important features of collisions which you need to remember. "Hard enough" refers to the total energy at the time of impact; "correct direction" refers to a suitable orientation of the colliding units. What makes for a suitable orientation? It depends. Somewhere along the way, specific atoms must make direct contact and there must be enough room for this to happen. Monatomics can act in any direction since they act as simple spheres and they are the same in any orientation. Polyatomics, however, may have limitations. For example, other atoms in the polyatomic unit may get in the way in some directions. Also, there can be an orbital component: specific orbitals can be involved in the reaction and, since most orbitals have a direction, then the collision may need to be along that direction. Overall, there are several underlying reasons for the need for suitable orientation. In the current example, the chloride ion is monatomic and spherical; the CH_3F molecule is polyatomic and tetrahedral, and it is different in different directions. For this reaction to occur, chloride must hit the carbon atom and that won't always happen. Let's consider several different directions for collisions.



First, let's say Cl^- smacks into the F atom in the molecule head on, as shown at left. What happens? Well, nothing. The fluorine atom blocks the chloride ion from hitting the carbon, so this is not a suitable orientation for reaction. The reactants simply bounce off each other and that is all.

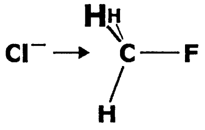


What if Cl^- collides with one of the hydrogen atoms as shown at right? This is also not a suitable orientation; this will give another bounce with no reaction.



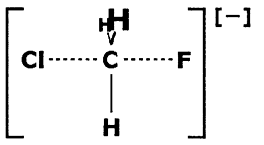
What if Cl^- comes in between two of the hydrogen atoms and the fluorine atom and hits the C as shown at left? Although this is now a direct hit by the Cl^- on the C, this won't work either due to orbital considerations. Sorry, still no reaction.

By the way, we set up this reaction as occurring in aqueous solution. We could consider the reaction in the gas phase but ionic reactions in the gas phase are not as common and, besides, they involve other interactions. Ionic reactions in aqueous solution are very common but solution reactions are complicated by the water molecules which are also present and which give hydration. Each CH_3F molecule and each Cl^- ion are surrounded and hydrated by water molecules, although those water molecules are not included in the pictures here for simplicity. In reality, reactants and solvent molecules are constantly jostling, bumping and shoving into each other, more forcefully at some times than at other times. In order for a reaction to happen, the Cl^- ion and the CH_3F molecule must jostle their way through the sea of water molecules and collide directly with each other.

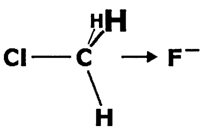


OK, there's been no reaction yet. What if Cl^- comes in from the other direction and slams into the C atom as shown at right? What happens? Well, that depends.

This collision has the correct direction but the collision must still be hard enough in order for the reaction to occur. Assuming that the collision does indeed carry enough impact, then the collision causes a distortion of the carbon's bonding. Three things happen: the incoming Cl^- ion pushes the hydrogens away and at one point they are flat with the C; a new covalent bond between chlorine and carbon starts to form; and, the bond between fluorine and carbon starts to weaken. This point of the process is drawn at left. This point is called the transition state or the activated complex. It is an energetically activated assembly which constitutes a key point in the transition from reactants to products.



This transition state is a very stressed out state. This is definitely not a favorable position to be in. Although five things are drawn attached to C, only the C–H bonds can be considered normal single bonds. The carbon is sp^2 hybridized at this point and the hydrogens are in the trigonal plane. Both the chlorine and the fluorine are trying to hang on but the best the carbon can do is work with its only remaining $2p$ orbital. There are simply too many things attached and everything is just too crowded. Something has to give, and that something is the fluorine which leaves as a F^- ion. Once this happens, you have a molecule of CH_3Cl product and the carbon is back to sp^3, tetrahedral, and once again content.



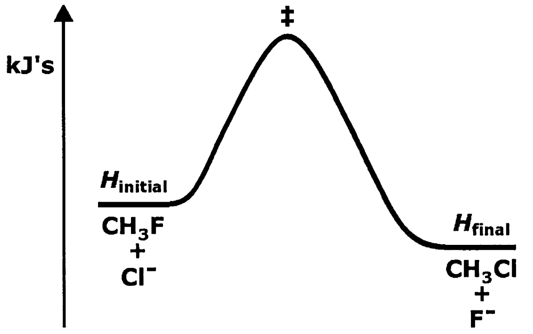
Let's summarize a few things here.

Collisions are fundamental to reactions. Not all collisions actually work to make product, however, and, in fact, most do not. Depending on the reaction and the conditions, only one in one thousand or one in one million or one in one billion collisions may actually result in a reaction. Oh, yes, there are some cases where most collisions result in a reaction but those situations are less common. In general, collisions must occur at sufficient energy and they must be in a suitable direction.

The requirement for sufficient energy is to get through that high energy transition state. This energy kick is not the energy of the reaction itself as given by $\Delta H°$ or $\Delta G°$ (ΔH or ΔG if nonstandard). The ΔH and ΔG remain completely defined by the initial and final states of the reaction. The transition state is a middle point and, as said again and again in the past, the middle does not matter to ΔH or ΔG. We can, however, use enthalpy or free energy to discuss the energy of the transition state itself; applied to a transition state, there is a special "double-dagger" notation, $H^\ddagger$ or $G^\ddagger$. We can also bring in the entropy of the transition state ($S^\ddagger$). Relative to the initial state of the system, all of these are connected by the usual relationship for free energy.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Although the above relationship connects with the prior four Chapters on thermodynamic parameters, we are going to simplify things and focus on the energy aspects without getting into the entropy side of the story. Furthermore, instead of using $\Delta H^\ddagger$ as our indicator of the energy requirement, we are going to take a more traditional approach in kinetics and work with a parameter called activation energy, designated by E_a. Technically, activation energy is the difference between the average energy of the reactant particles and the average energy of the transition state particles which are forming product. Conceptually, E_a is the measure of the energy which is needed to get to and through the transition state.

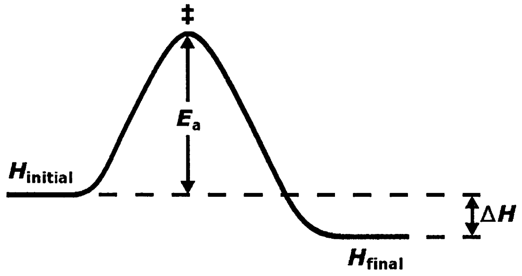


At left is a diagram of energies related to the present system at various stages of this reaction. The vertical scale is the energy, simply illustrated as kJ's. (The vertical scale is shown here but will not be shown in later diagrams.) The left end of the curvy plot shows the total enthalpy of the initial particles (CH_3F and Cl^-), given as the initial enthalpy $H_{initial}$. At the right end of the plot lies the final enthalpy of the system H_{final} which represents the total enthalpy of the product particles (CH_3Cl and F^-). The center of the plot shows the energy of the stressed-out transition state, simply shown as ‡. Notice that this is a sizeable energy bump which must be overcome in order for reactants to react to produce products. The energy bump is considerable for this reaction; other reactions may have one smaller or larger. This kind of plot is called a reaction energy diagram, R.E.D., and the meaning of the plot is as follows. Assuming the Cl^- ion collides into the CH_3F molecule in a suitable direction, the impacting pair can undergo a distortion; this distorted state has a higher energy than the energy of the initial particles. As the distortion intensifies, the energy increases. If the hit is hard enough, the distortion can reach the transition state, ‡, which represents the highest point of energy on the curve. Going past this point, the chloride becomes fully bonded as fluoride is ejected, thus removing the distortion and lowering the energy to that of the final products. All of this happens extremely fast, in a mere nanoblink of the eye (nanoseconds range).

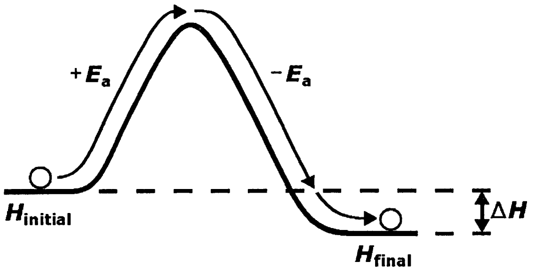
As always for any reaction, we can write

$$\Delta H = H_{final} - H_{initial}$$

and this is the change in enthalpy for the reaction at any given conditions. This particular reaction is exothermic with $\Delta H° = -23$ kJ. Notice in the plot that the system ends at lower energy than it started, since some energy is released to the surroundings. While ΔH is for the reaction overall, E_a is the energy needed to reach the transition state from the initial state. For this reaction, $E_a = 90.$ kJ. The pictorial representations of ΔH and E_a are shown in the R.E.D. at right for this reaction.



(By the way, the symbol E_a does not take a Greek delta, although it is a difference in energies like a ΔH. In other words, it is simply written E_a and not ΔE_a. That's just the way the symbol was set up years ago and that way has stuck.)



Notice that the reaction is exothermic and releases energy overall, but there is still an energy barrier to overcome. A useful analogy is a ball rolling up a hill and rolling down the other side, ending lower than where it started. Gravity wants the ball at the lower position, but it needs a kick to get over the hill first. The energy of the kick must provide $(+)E_a$ to get up the hill, but that same amount is recovered as $(-)E_a$ once it rolls down to the height at which it started. This E_a has no net effect in the end because energy-in equals energy-out to this point in the process. After that point, however, it rolls to the final level, releasing more energy. That additional amount is the net change and corresponds to the ΔH for the reaction. This behavior is typical for reactions: regardless of exothermic or endothermic, most reactions will require some initial kick in order for reactants to react to produce products. That energy is commonly provided by the thermal energy of the system at whatever temperature it happens to be; that thermal energy provides for a range of motions including collisions between the various particles involved. On the other hand, that energy can instead be provided by electromagnetic radiation (light), which then becomes the basis for photochemical reactions such as the types involved in photosynthesis or your vision. (Remember the excited state business of Section 21.2? We can now say that the photons are providing the payment for some E_a.) In general, the height of the energy bump is a major factor in how fast a reaction will proceed. All of this still assumes that the collisions are in the correct direction. If the direction is completely wrong, then the energy of the impact means nothing. If the direction is correct but the energy is not enough, then there will be some distortion of the reactant molecule but not enough to get to and through the transition state; the particles will end up bouncing off each other with no reaction.

Overall, this description for the reaction of Cl^- with CH_3F constitutes the mechanism for the reaction. Of the many different types of mechanisms, some, such as this one, occur in one single step; other reactions can occur in two or even many steps. In addition to the number of steps, we can also consider the "molecularity" of each step. Molecularity is a very important concept in kinetics. The molecularity of a step is the number of particles which undergo chemical change in that one step. The particles can be molecules, ions or just single atoms. If one particle is reacting by itself, the step is called "unimolecular". If two particles collide and react together, then the step is "bimolecular". If three particles collide and react, then the step is "trimolecular" (also called "termolecular"). Threesomes are much less common than doubles because a collision of three things at the same time just doesn't happen nearly as often as a collision of two particles. Three is the highest molecularity because higher numbers of particles simply do not collide all at once. In the present case of $CH_3F + Cl^-$, one molecule of CH_3F and one ion of Cl^- collide and react. Since two particles are involved, this reaction is bimolecular.

Next Example.

- SECOND EXAMPLE

We will now consider another reaction which also produces chloromethane, but now in the gas phase using different reactants and a totally different mechanism. The balanced equation for this process is

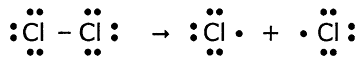
$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

but this is an overall reaction which actually occurs in several steps. $\Delta G°$ for the overall reaction is −104.77 kJ, so it is quite exergonic.

‣ Step 1 $Cl_2(g) \rightarrow 2\ Cl(g)$

Given a big enough kick, a molecule of Cl_2 breaks its single σ bond to produce two atoms of Cl. This is not a trivial task, however, given that the bond energy of Cl_2 is a sizeable 248 kJ/mol. This reaction is very endergonic at standard conditions at 25 °C, with $\Delta G° = 210.62$ kJ. This job takes high temperatures at which $\Delta G°$ is smaller and at which there is more thermal energy available. Even then, however, the energy barrier is still too large (~200 kJ at 1200 °C) for a single molecule to break apart on its own at an appreciable rate. But there's a catch: keep in mind that these gas-phase molecules are flying wildly about and colliding with other molecules, some with more energy than others. When two molecules collide at the higher temperatures, the <u>combined</u> energies can cause one molecule to break its bond while the other molecule stays intact and bounces off. Thus, one molecule breaks up at a time, but it still requires a collision with some other particle. That particle can be another molecule of Cl_2, a molecule of CH_4 which is also present, etc. It can even be some nonreacting particle which may be present in the system, such as He or Ar. In kinetics, a nonreacting collider molecule (or atom) is symbolized by M. Although M is physically involved, it does not undergo chemical change and only the molecule of Cl_2 is reacting. Since only one molecule is reacting, this Step is unimolecular. Although a collider M is required for a unimolecular step in the gas phase, it is not a universal requirement for other reactions. In fact, most bimolecular and all trimolecular gas phase reactions do not involve any M. In solution, the solute and solvent are constantly bumping and kicking each other anyway; those constant collisions provide added energy in a solution reaction. Although M is needed in some cases, it will not be our primary focus and I will usually just leave it in the background for the majority of coverage here. I include M here (and in Step 4 below) as a further illustration of the importance of energies, motions and collisions.

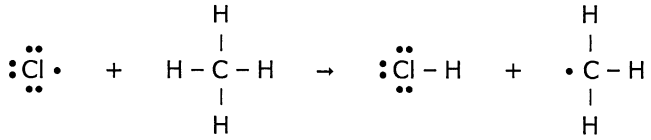
Instead of picturing molecular shapes and R.E.D.s this time, we will look at Lewis structures in order to highlight some additional aspects. Consider the one molecule which breaks its bond in this Step.



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

Each chlorine atom on the right has one odd electron which is unpaired; each atom is therefore paramagnetic and a free radical (a term first used back in Section 26.1). Why is this important? Paramagnetics can react very differently than diamagnetic chemical units (as first mentioned in Section 24.3) and this provides additional avenues for the mechanisms which are possible. Furthermore, most (not all) free radicals are very energetic and very reactive species, especially at higher temperatures.

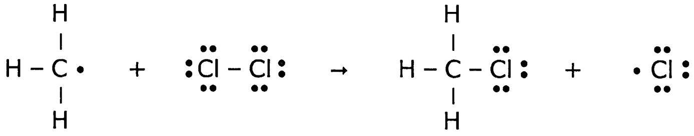
▸ Step 2 $Cl(g) + CH_4(g) \rightarrow HCl(g) + CH_3(g)$



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + H-\underset{H}{\overset{H}{C}}-H \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-H + \cdot\underset{H}{\overset{H}{C}}-H$$

A chlorine atom from Step 1 collides with a molecule of CH_4. For those collisions which have sufficient energy and suitable orientation, the Cl atom pulls one H off the CH_4 molecule; this forms a product molecule of HCl and a CH_3 unit. This is a bimolecular step. The HCl molecule is diamagnetic but the CH_3 unit has an unpaired electron and is paramagnetic. This free radical, CH_3, goes by the name methyl radical. It is also very energetic and very reactive. This Step is energetically mild compared to Step 1, with $\Delta G° = -1.98$ kJ and $E_a = 11$ kJ, both of which are very small.

▸ Step 3 $CH_3(g) + Cl_2(g) \rightarrow CH_3Cl(g) + Cl(g)$



$$H-\underset{H}{\overset{H}{C}}\cdot + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow H-\underset{H}{\overset{H}{C}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

The methyl radical from Step 2 collides with a molecule of Cl_2 and, if done with sufficient energy and in a suitable orientation, another bimolecular step occurs. "Sufficient energy" is even easier here than in Step 2, since $E_a = 4$ kJ which is very, very small. This Step is quite exergonic at 25 °C with $\Delta G° = -102.79$ kJ. This Step produces a molecule of chloromethane along with another chlorine atom. The chloromethane is diamagnetic; the chlorine atom, however, like the chlorine atoms from Step 1, is paramagnetic and very reactive. These Cl atoms can collide and react with other molecules of methane as in Step 2, or they can do Step 4.

▸ Step 4 $2\ Cl(g) \rightarrow Cl_2(g)$

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

This is the reverse of Step 1 and again some collider M will be required but now for a different reason. Ironically, since chlorine atoms are so very energetic, a collision of two is <u>too</u> high in energy for a bond to grab hold; instead, the atoms collide and fly apart. On the other hand, if two atoms of Cl and one other molecule M collide all at once, then M can absorb more of the energy of the impact, thereby allowing the two Cl atoms to stick together and form a new molecule of Cl_2. In this process, the two free radicals of Cl combine to form a diamagnetic molecule of Cl_2. Since two particles are reacting, this is a bimolecular step. Because this Step involves too much energy of collision, it has no energy barrier. There is also very little orientation requirement during the collision since two monatomics and a simple collider are involved. Thus, collisions of this type will have very high success in producing another molecule of Cl_2. But, as noted earlier, close encounters of the third kind just don't happen nearly as often as two-way collisions.

This is the breakdown of the four Steps in the mechanism for this reaction. As the reaction proceeds, all four Steps are happening at the same time. Step 1 gets the action going by producing some Cl atoms for Step 2. Step 2 produces the CH_3 radical needed for Step 3. Step 3 produces another Cl atom which can go back into Step 2. Steps 2 and 3 actually form a chain loop and they can continue on and on until something breaks the chain. For example, running out of reactants will break the chain. Step 4 will also interfere with the chain by using up Cl atoms. Steps 2 and 3 are actually called chain steps; these are the most important since they can happen hundreds or thousands of times more often than Steps 1 and 4. Furthermore, Steps 2 and 3 are the ones which produce the HCl and CH_3Cl product molecules. Steps 1 and 4 do not give any HCl and CH_3Cl, but they are still part of the mechanism and they still affect the overall speed of the whole process.

As you can see, this Second Example is much more complicated than the First Example since there are now several Steps. I've provided a bit of detail for this Example to show additional aspects which can be involved. Yes, four steps can get complicated, but some reactions have 20 or more steps.

These Examples illustrate two common types of mechanisms. Although these two are common, there remain plenty of other mechanisms, some common and some not so common.

48.3 It's elementary.

Most chemical reactions are not just one step; instead, they are composites of two or more mechanistic steps. As such, those reactions are called composite reactions or we say they have composite mechanisms. For those reactions which are composed of only one step, the term is simple mechanism. Thus, the First Example involves a simple mechanism while the Second Example involves a composite mechanism. In a composite mechanism, each step will have its own different E_a and its own different rate. The overall rate for the composite reaction as a whole will depend on the individual rates of the individual steps. In some composite mechanisms, one step will stand out as much slower than the other steps and that simplifies things. In these cases, the overall rate depends on the rate of that one, very slow step and that step is called the rate limiting or rate determining step.

Each individual step in a mechanism is called an elementary step. This is a very important term which you need to understand. An elementary step is a specific mechanistic step which conveys the specific action on a particle-to-particle basis of who is doing what to whom. The reactants given in the equation for an elementary step will only include those chemical units which are reacting in that step. As such, the reactants give us the molecularity of the step. Each of Steps 1 - 4 in the Second Example are elementary steps. Each equation for each Step only gave the molecules (or atoms) which were directly reacting in that Step. The overall equation, however, was

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

and that tells us the mole-to-mole relationships for all reactants and all products over the course of the overall process. We need that overall reaction for stoichiometry but, if we want to know how the reaction works, then we must examine the elementary steps. The overall equation tells us the net, overall outcome after all elementary steps are done; as such, the overall equation can be depicted as the sum of the individual steps. Here, Steps 2 and 3 are operating many times more than Steps 1 and 4, so we can't just simply add up all four Steps equally. Fortunately, Steps 1 and 4 are the reverse of each other, so these two cancel overall.

$$\begin{array}{ll} \text{Step 1:} & Cl_2(g) \rightarrow 2\,Cl(g) \\ \text{Step 4:} & \underline{2\,Cl(g) \rightarrow Cl_2(g)} \\ \text{Sum:} & \text{(cancel)} \end{array}$$

Steps 2 and 3 then add up for the overall result.

Step 2: $Cl(g) + CH_4(g) \rightarrow HCl(g) + CH_3(g)$

Step 3: $CH_3(g) + Cl_2(g) \rightarrow CH_3Cl(g) + Cl(g)$

Sum: $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

This summation parallels the additivity of reactions going back to Section 6.4. We cancel out identical items on both sides of the balanced equation for the overall reaction. This includes all of the free radicals involved, and this means Cl and CH_3 do not appear in the overall equation. These are intermediates, a term first used also back in Section 6.4. For a composite mechanism, an intermediate is any chemical unit which is produced in one elementary step but used up in a later step; these cancel out in the final summation and do not appear in the overall balanced equation.

CAUTION! As we go along here, be aware that we are considering balanced equations which represent elementary steps and balanced equations which represent an overall process. For purposes of kinetics, this distinction can be important. If presented with an equation, you may need to know whether it is elementary or overall. Sometimes they are the same but usually they are different. They are the same for simple mechanisms such as the First Example. For the Second Example, however, the overall reaction and the elementary steps were all different. How will you know whether a given equation represents an overall process or a single elementary step? For one thing, watch the wording. In the above equations, these were said to be elementary. For another thing, elementary equations convey molecularity and overall equations do not. Since there are only three cases of molecularity (unimolecular, bimolecular and trimolecular), an elementary equation can only have one, two or three particles shown on the left. If you are given an equation with one, two or three reactants, then it may be elementary or it may be overall. If you have an equation with four or more particles indicated on the left, then it is not elementary and it must be an overall equation. Also, if you have an equation with a fractional coefficient, then it is not elementary. Elementary equations must have whole numbers for coefficients since these convey chemical detail; a fraction of a molecule has no meaning at this level of detail.

Consider the following examples.

- $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

  Only one molecule is indicated on the left. This equation could represent an elementary step or it could represent an overall reaction. We cannot tell from just this much.

- $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

  A total of three molecules are indicated on the left. This equation could represent an elementary step or it could represent an overall reaction. Again, we cannot tell from just this much.

- $H_2O_2(aq) + 2\ I^-(aq) + 2\ H^+(aq) \rightarrow 2\ H_2O(l) + I_2(s)$

  This equation has a total of five particles indicated as reactants. This exceeds any possible molecularity, so it cannot be an elementary step and it must be an overall equation.

Be mindful of these points.

OK, we've just laid down a number of very important aspects for mechanisms. Let's summarize some of these.

- All reactions are composed of one or more elementary steps. If only one step is involved, then the process is described as simple. If two or more steps are involved, then the process is described as composite.

- In most cases, each elementary step will have an energy barrier to overcome in order for the reactants of that step to form products. The energy to get over this barrier, E_a, derives from thermal energy, and/or collisional energy, and/or EM radiation. This E_a is a separate issue from the ΔH of the reaction for that step.

- The molecularity of an elementary step refers to the number of particles which are reacting in that step. For a unimolecular step, one particle is reacting. Likewise, for a bimolecular or trimolecular step, two or three particles are reacting. Note: molecularity is the number of particles reacting and not necessarily the number of particles colliding. Nonreactive colliders (M) are not a part of molecularity.

- By itself, the balanced equation for an overall reaction does not tell us anything about the mechanistic steps. The overall balanced equation is ultimately derived from all elementary steps involved. There may be only one elementary step or there may be many.

- The speed of the overall reaction will depend on the various speeds of the individual steps. It is possible for one step to stand out as much slower than the rest. The slowness of this step then dominates the overall speed.

The above is fairly general to a wide number of reactions.

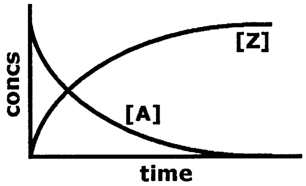
The discussion so far has dealt with mechanistic aspects. Now, let's get into the speed aspects.

48.4 Speed relationships

The speed of a reaction is simply how fast it goes. This is measured by how fast the reactants are disappearing or how fast the products are appearing. For a general illustration, consider a very simplistic reaction of compound A reacting completely to form compound Z in a one-to-one relationship.

$$A \rightarrow Z$$

The diagram at right plots the concentrations of A and of Z at the start time (zero) and progressing through a period of time which represents completion of the reaction. Compound A starts at some initial concentration and decreases with time to zero. Compound Z starts at zero initial concentration and increases with time until it reaches its final amount. The speed along the way is determined by the change in concentration of A or of Z over some period of time. At the start of that period of time, you have some initial concentration $[\ ]_{\text{initial}}$ and at the end of that period of time you have a final concentration $[\ ]_{\text{final}}$. The difference, Δ, is final minus initial.



$$\Delta[A] = [A]_{\text{final}} - [A]_{\text{initial}}$$

$$\Delta[Z] = [Z]_{\text{final}} - [Z]_{\text{initial}}$$

We set up this reaction as a one-to-one mole-to-mole relationship in the balanced equation above; in such a case, the change in the moles of A which are present is equal to the change in the moles of Z present, although the changes are of opposite sign. Since A and Z are in the same container, then they have the same volume; mole-to-mole is the same as (mol/L)-to-(mol/L), which is the same as concentration-to-concentration. The overall result is that Δ[A] and Δ[Z] have the same numerical value, except they are going in opposite directions: [A] is decreasing so Δ[A] is negative, and, [Z] is increasing so ΔZ is positive.

$$-\Delta[A] = \Delta[Z]$$

For speed, we want the change in concentration over some period of time, Δt.

$$\text{speed (rate)} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[Z]}{\Delta t}$$

(Note that time gets lower case *t*. Temperature will stay capital *T*.) Again, Δ[A] takes a negative sign and Δ[Z] takes a positive sign. This will be true for speed relationships in any reaction: reactants will get a negative sign and products will get a positive sign.

If you're into calculus, these speeds are treated as derivatives (such as $d[Z]/dt$) and they are the slopes of the curves in the plot illustrated above. Calculus pops up in several places in the handling of kinetics, but we will not deal with calculus here. For our purposes, the Δ notation will suffice.

In most cases, the speed of the reaction slows down with time since the amounts of reactants are decreasing with time. This can be seen in the plot above where the curves start fairly steep (down for A, up for Z) but level off after a while. The steep parts mean large changes in concentrations are occurring per time and that represents a fast speed. The more level parts mean small changes are occurring per time and that represents a slower speed.

The example here involving one mole of A reacting to form one mole of Z is the easiest to illustrate, but most reactions are more complicated. That will then give more complicated speed relationships. Let's do a specific example with all coefficients of one; keep in mind that reactants get a negative sign while products get a positive sign. Returning to the equation from the First Example,

$$CH_3F(aq) + Cl^-(aq) \rightarrow CH_3Cl(aq) + F^-(aq)$$

we can set this up as follows. Over some time interval, all concentrations change on a one-to-one-to-one-to-one basis.

$$-\Delta[CH_3F] = -\Delta[Cl^-] = \Delta[CH_3Cl] = \Delta[F^-]$$

In other words, as some concentration of CH_3F reacts, the same concentration of Cl^- reacts, while the same concentration of CH_3Cl and of F^- are produced. As long as all coefficients in the balanced equation are one, then all relationships here are also one. Incorporating a time interval, Δt, we can write the rates of change in concentrations of each component.

$$\text{speed (rate)} = -\frac{\Delta[CH_3F]}{\Delta t} = -\frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[CH_3Cl]}{\Delta t} = \frac{\Delta[F^-]}{\Delta t}$$

This says that the speed of the reaction can be expressed by how fast the concentration of either reactant or either product is changing.

When one or more coefficients of the balanced equation are other than one, then you need to incorporate the coefficient into the relationship, except the coefficient gets inverted. For an illustration, consider the industrial process used to make ammonia.

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

This balanced equation says one mole of N_2 reacts with three moles of H_2 in the same time. Thus, the amount of hydrogen reacting is three times faster than the amount of nitrogen reacting.

$$-\Delta[H_2] = 3 \times (-\Delta[N_2])$$

or

$$\frac{1}{3}(-\Delta[H_2]) = -\Delta[N_2]$$

By a similar consideration, one mole of nitrogen reacts to form two moles of ammonia in the same time; ammonia forms twice as fast as the nitrogen reacts.

$$\Delta[NH_3] = 2 \times (-\Delta[N_2])$$

or

$$\frac{1}{2}\Delta[NH_3] = -\Delta[N_2]$$

Putting these together, we have

$$-\Delta[N_2] = -\frac{1}{3}\Delta[H_2] = \frac{1}{2}\Delta[NH_3]$$

and the speed relationship is

$$\text{speed (rate)} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

This says that the speed of the reaction can be expressed numerically in terms of any reactant or product, incorporating the inverted coefficients from the balanced equation.

We can generalize all of these speeds as follows. For some generic equation between A and B to produce Y and Z and where a, b, y and z are the coefficients,

$$a\,\text{A} + b\,\text{B} \rightarrow y\,\text{Y} + z\,\text{Z}$$

then the speed relationship for the reaction is the following.

$$\text{speed (rate)} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{y}\frac{\Delta[\text{Y}]}{\Delta t} = \frac{1}{z}\frac{\Delta[\text{Z}]}{\Delta t}$$

Just remember that reactants take a negative, products take a positive, and all coefficients from the balanced equation go in upside down.

Let me make two points.

The first point is that we will only work with gases and solutes in our speed relationships. Both of these can be expressed as concentrations and that will be our principal unit. We will not work with solids or liquids in the speed relationships since they do not relate to a concentration. Of course, you can work with the amounts of solids or liquids by the usual stoichiometric connections if you really need to.

For the second point, there is a catch to note. The numerical value for speed will depend on how the coefficients are written in the balanced equation. To illustrate this point, consider the formation equation for ammonia. Since formation equations are defined for one mole of product, this will have different coefficients than the equation written above.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

For this format, the speed relationship still uses the inverse coefficients but now it is written differently from the one above.

$$\text{speed (rate)} = -2\frac{\Delta[N_2]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[NH_3]}{\Delta t}$$

This is somewhat of a minor detail for now but there are consequences to this in some of the math. This aspect has parallel in thermodynamics, where the values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ also depend on how the reaction is written. Now in kinetics, the numerical values for rate relationships will also depend on how the equation is written.

So far, the speed relationships tell us how fast things are changing along the way. As previously noted, the speeds themselves are usually changing during the course of a reaction because the concentrations are changing. It is possible to experimentally measure the connection between speed and concentration. These connections are very important. For example, if we know the connection between a reaction's speed and one set of conditions, then we can calculate a speed for another set of conditions; this can also lead to the timeframe for how long a reaction may take for some given starting conditions. For another example, these experimental measurements of speed can guide us to understanding the mechanism for some process. We will see some of these things as we continue.

Problems

1. True or false.
   a. Every collision between reactant particles produces a molecule of product.
   b. The elementary step given by $Br_2(g) \rightarrow 2\,Br(g)$ is unimolecular.
   c. A composite mechanism is composed of two or more elementary steps.
   d. The reaction given by $P_4(s) + 6\,H_2(g) \rightarrow 4\,PH_3(g)$ cannot be elementary.
   e. An intermediate in a composite mechanism does not appear in the balanced equation for the overall reaction.
   f. Every trimolecular mechanism has three elementary steps.
   g. The speed of a reaction typically increases as the reaction progresses.

2. Write the speed relationships between reactants and products for each of the following.
   a. $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$
   b. $HS^-(aq) + 3\,ClO^-(aq) \rightarrow HSO_3^-(aq) + 3\,Cl^-(aq)$
   c. $CH_2Cl_2(g) + 2\,H_2O(g) \rightarrow CO_2(g) + 2\,HCl(g) + 2\,H_2(g)$