

CPC 022

DAY 8

*Rate and
Equilibrium*

Dr. Olivieri

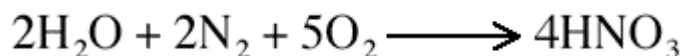


Percy Lavon Julian

The news is flooded with steroid use accusations these days. It seems as if athletes can't get enough of the juice. Percy Lavon Julian was a chemist during the beginning of the 20th century who worked with the synthesis of natural steroids, which later led to the mass production of steroids. He also worked with the structural similarities between sex hormones, bile acids, and cortical hormones. Kick all your learning chemicals into gear...you are almost done!

- **Rates**

The reaction:



is extremely exothermic. According to this equation, the world's oceans should long ago become a gigantic reservoir of nitric acid. That they have not is a testament to the importance of reaction rate.

Even though this reaction is very exothermic it proceeds extremely slowly. Much too slowly to be noticeable amongst all the other reactions, that take place everyday in the atmosphere and in the world's oceans. The fact that a reaction can proceed spontaneously does not mean that it will occur rapidly, and the study of these factors that influence the speed of a chemical reaction is called "reaction rates".

- **Idea of kinetics**
Kinetics

If you start with a chemical reaction, for example the decomposition of hydrogen peroxide:



The study of kinetics asks first and foremost, "how fast does the hydrogen peroxide disappear; how fast does molecular oxygen and water appear?" It then asks the related question, "What can be done to speed up or slow down this reaction?" A scientist may find that changing the concentration of hydrogen peroxide may influence the rate. Or he or she may find that some additive of some sort may speed things up. For example, a drop of blood added to a bottle of peroxide will cause it to rapidly froth. What's going on here?

The third question is the generic why. Why do some reactions go faster than others? Why do all reactions go faster when you heat them up? Why do some additives make peroxides decompose, while others seem to be inert?

So the three questions we ask in kinetics are:

- How fast do reactions go?
- What can we do to change the speed of a reaction?
- Why?

- **Finding rates is empirical**

While there are many theories about reaction rates, there are no simple rules to predict how fast a particular reaction will go, or to predict precisely what we must do to influence its rate one way or another. Chemical kinetics is empirical, by this we mean that the results are almost wholly derived from experimentation. Each reaction must be studied on a case by case basis.

- **Factors that influence reaction rate**

The central question of chemical kinetics is "What can we do to speed up or slow down a reaction?". Chemists have found that one of the following is most likely to influence the rate of reaction:

- Temperature
- Reactant concentration
- Presence of a catalyst

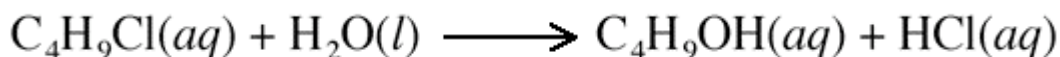
- **Dependence on Temperature**

In general, heating up a reaction makes the reaction go faster. This is because adding heat increases the average energy of the molecules: they hit each other more frequently and they hit each other harder.

- **Dependence on Concentration**

There are few, if any, generalizations that can be made about the dependence of reaction rate on concentration. It is, as noted elsewhere, something that must be studied empirically. Usually increasing the concentration of the reactant, will speed up a reaction, but even this is not always true.

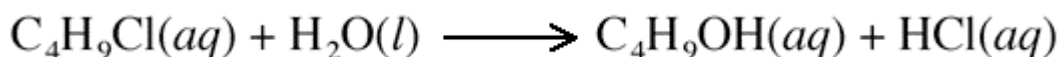
But even "when the concentration increases, the rate increases" is not by any means the entire story. For example, in the reaction of butyl chloride with water:



Does doubling the concentration of butyl chloride double the reaction rate? Does it quadruple it? This is something that we find out experimentally.

- **Order of reaction**

The precise mathematical dependence of rate on concentration is known as the order of reaction. Consider the reaction we talked about on the previous page:



Suppose we find out that when we double the butyl chloride concentration the reaction rate doubles; that when we triple the butyl chloride concentration the reaction rate triples. This situation, where the reaction rate "follows" the concentration is called first order kinetics.

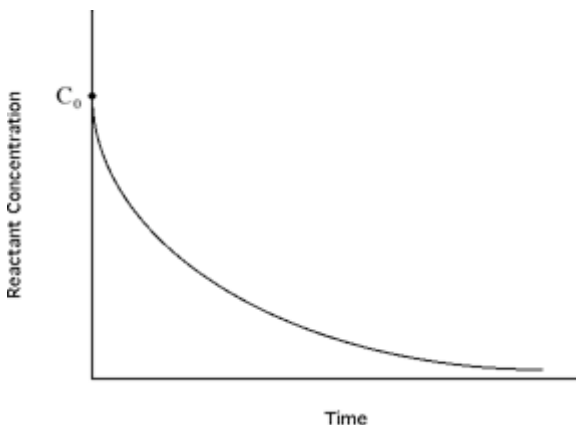
But suppose we found that when we doubled the butyl chloride concentration the rate quadrupled; when we tripled it the rate went up by a factor of nine, quadrupled it and the rate went up by a factor of sixteen. This is called second order kinetics because $2^2 = 4$, $3^2 = 9$, $4^2 = 16$. In second order kinetics the rate is proportional to the concentration raised to the second power. You can have any imaginable order for your kinetics-- you can't predict ahead of time how it should come out-- you have to run the experiment.

For the current reaction it turns out that the reaction is first order in butyl chloride.

▪ Graphing 1st order rates

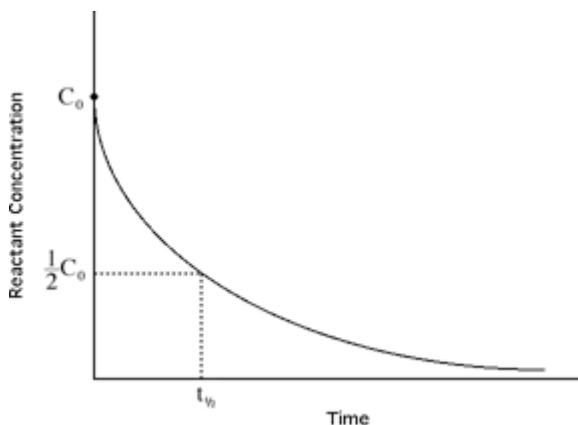
First order kinetics are, by far, the most important and ubiquitous found in nature. The rate at which a hot teakettle cools, the rate at which radioactive isotopes decay, the rate at which the image of a bright lamp filament disappears from your eye, as well as the rate at which alcohol, marijuana or other more therapeutic drugs leave your system, all are governed by first order kinetics and all exhibit the same kind of behavior.

In first order kinetics, the concentration of the reactant, which is behaving in a first order fashion, always exhibits exponential decay.



Note how in exponential decay the graph intercepts the y-axis. It has to for this to make physical sense, because we have to start the reaction with some finite amount of reactant (which we have labeled C_0). Note how the graph approaches the t-axis asymptotically. It gets closer and closer to zero but it never quite gets there.

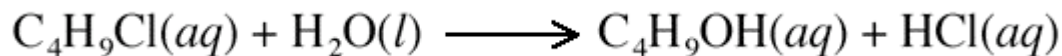
All first order reactions are characterized by a quantity known as half-life, the time it takes some initial concentration to decline to one-half its initial value. Fast reactions have very short (small) half-lives. Slow reactions have very long half-lives.



▪ Rate laws

The mathematical expression for the dependence of rate on concentration is called a rate law. This term is misleading because the word "law" implies that there is something fundamental or transcendental about a rate law. Nothing could be further from the truth; we must discover the rate law for each reaction. As noted elsewhere, kinetics *is* empirical.

As an example, consider the butyl chloride reaction:

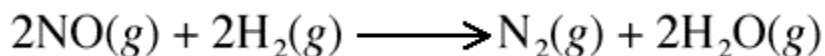


It turns out that this reaction is first order in butyl chloride and does not depend on the concentration of water (another way of putting this is that it is zeroth order in water). The rate law for this reaction would be written as follows:

$$\text{Rate} = k[\text{C}_4\text{H}_9\text{Cl}]$$

In this equation k is called the rate constant, it is not the same thing as the rate. The brackets around the butyl chloride mean "concentration of". The concentration of butyl chloride is raised to the first power (the absence of any exponent implies this) and, this is because, the reaction is first order in butyl chloride.

In the reaction:



it is experimentally determined that the rate is second order in NO and first order in hydrogen. We would write the rate law for this reaction as follows:

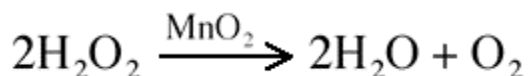
$$\text{Rate} = k[\text{H}_2][\text{NO}]^2$$

We say that the overall order of this reaction is third order (2+1=3). Note that the rate constant, k , is highly unlikely to have the same value as k for the butyl chloride reaction, or k for any other reaction. Every reaction has its own rate constant.

- **Catalysis**

Catalysts

Catalysts are substances that speed up chemical reactions, but are not themselves consumed. In the decomposition reaction of hydrogen peroxide:



manganese dioxide, the substance written above the reaction arrow, acts as a catalyst. An open beaker of 3% hydrogen peroxide will slowly, almost imperceptibly, evolve oxygen. If a small amount of manganese dioxide is added the peroxide bubbles and froths. Oxygen is being rapidly evolved. When the reaction ends, close examination of the beaker will reveal that all of the manganese dioxide remains at the bottom, un-reacted.

Catalysis are used in all sorts of industrial applications; the manufacturing of Crisco from vegetable oil, the polymerization of Plexiglas, the removal of nitrogen oxides from the exhaust of internal combustion engines, to name but a few.

- **Enzymes**

All biological systems contain special catalysts known as enzymes. If you take that 3% peroxide solution and add a drop of blood to it, the effect will be as dramatic as the addition of manganese dioxide. The peroxide will froth and bubble and oxygen gas will be rapidly evolved.

The reason for this is the presence of an enzyme (a biological catalyst) called peroxidase, which is always present in our bodies in order to rid us of potentially toxic peroxides.

Most enzymes are large protein molecules whose shapes fit the shapes of the molecules that they induce to react. After the reaction takes place, the enzyme remains intact, ready to move on to the next set of molecules, like any good catalyst. There are innumerable enzymes in the human body each promoting some specific (and generally important) biochemical reaction.

- **Collision theory**

Collision theory attempts to explain the results of kinetics experiments in terms of the individual atoms and molecules that are undergoing chemical reaction. Specifically, collision theory explains the temperature dependence of reaction rates, as well as some aspects of the behavior of catalysts.

Collision theory recognizes that, for a reaction to take place, at least three conditions must be met:

1. A collision must take place.
2. The participants in the collision must be oriented in such a way that a reaction can take place.
3. A collision must be sufficiently energetic for it to result in a chemical reaction.

- **Collision frequency**

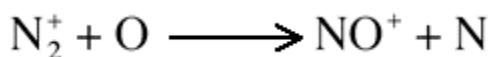
For a chemical reaction to take place the molecules must collide. Even if the reaction involves the decomposition of a single molecule, that molecule must have collided with something to give it the energy necessary to decompose. It is reasonable to expect that the reaction rate will depend on the collision frequency: the greater the number of collisions per second, the faster the rate of reaction.

The easiest way to increase the collision frequency is to turn up the heat. At higher temperatures, the average molecule travels faster than

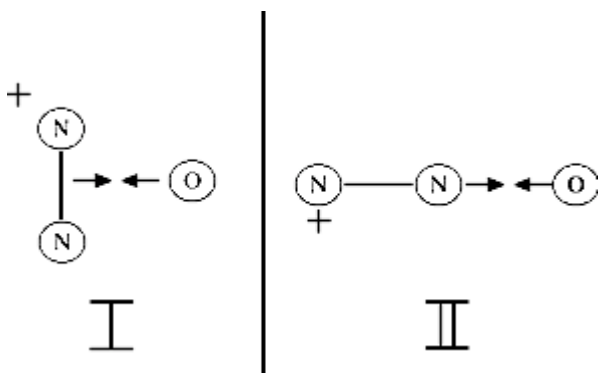
it does at low temperatures. Faster molecules mean higher collision frequency, which in turn, means faster reaction rate.

- **Steric factor**

Even if a molecule collides with another molecule, there is no guarantee that this collision will result in a chemical reaction. Consider the following gas-phase ionic reaction that takes place in the upper atmosphere:



It is not clear that every collision will have the proper orientation for a reaction to take place. In the above reaction we can think of at least two very different methods of approach:



It is conceivable, but very unlikely, that the broadside attack (I) and the end-on approach are equivalent in promoting the reaction. There is no way to say in advance which one leads more readily to reaction but in most cases it is likely that one or the other will be highly ineffective. If this is the case then not all collisions will result in a reaction.

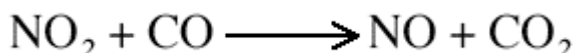
The steric factor is simply a number between zero and one, which says, "This is the fraction of all collisions which have the proper orientation for a reaction to take place."

- **Energy of activation**

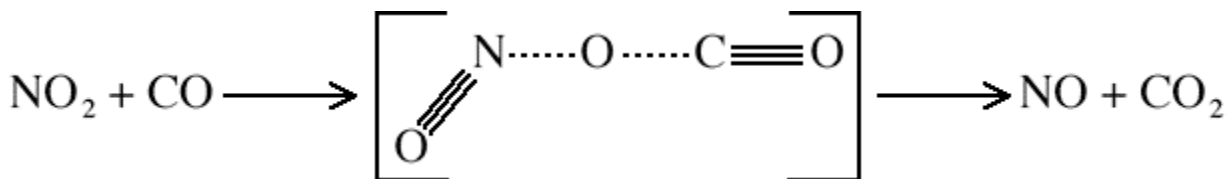
Activation Energy

Even if the reactants collide and even if the collisions have the right orientation, a reaction will not take place unless the molecules get close enough to each other for the old bonds to break and the new bonds to form. The "outer crust" of all atoms and molecules consist of electrons. These repel each other because they are all negatively charged. The trick is to squeeze the molecules close enough together so that the new bonds (the bonds that will hold the products together) can form.

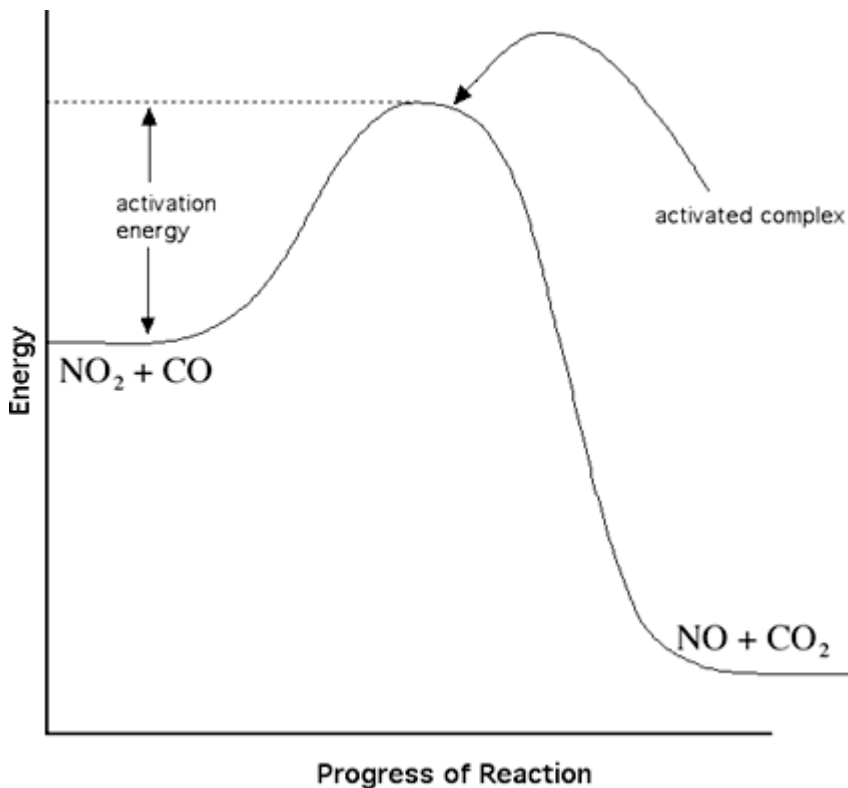
The energy needed to squeeze the molecules close enough together is called the activation energy. We can provide this activation energy by providing heat to the molecule. Consider the reaction in which carbon monoxide abstracts an oxygen from nitrogen dioxide:



For this reaction to take place, the carbon monoxide molecule must get close enough to the nitrogen dioxide for a new C-O bond to form, and, simultaneously for the old N-O bond to break.



The intermediate "supermolecule" that represents the transition between reactant and product is called the activated complex. Obviously you have to push the reactants together to make this complex happen, and to do this you are going to have to provide energy. This energy is called the activation energy and its origins are depicted schematically below.



- **Catalysis**

Activation Energy: Catalysts

It is believed that catalysts work by lowering the activation energy, increasing the steric factor, or both. When, for example, reactant molecules are adsorbed on the surface of a solid catalyst, the catalyst influences the distribution of electrons such that the reactants can approach each other closely without requiring large kinetic energy.

In some cases, the chemical structure of the catalyst may be, such that, the molecules are oriented relative to each other in a manner conducive to reaction. When this happens, in effect, the steric factor is increased. In other words, virtually every pair of reactants attached to the surface of the catalyst is oriented correctly.

So catalysts can speed up reactions in two ways:

1. They can lower the activation energy,
2. They can properly orient reactants, thereby increasing the steric factor.

- **Enzymes**

Activation Energy: Enzymes

Enzymes, being biochemical catalysts, function in much of the same way as conventional catalysts. They lower the activation energy for biochemical reactions.

The activity of enzymes is very specific. Generally, enzymes are shaped in such a way that only a very narrow range of molecules can attach themselves to them: in other words, enzymes are extremely specific about which reactions they catalyze. This specificity is extremely important in living systems, where in general, a single specific reaction is desired, and any other side reaction would be useless or harmful to an organism.

The activity of enzymes has been compared to a lock and key: the enzyme is the lock, and only one particular key will fit. Clearly, such spatial selectivity also has a built in orientational (steric factor) bias. For example, a specific enzyme, lactase, is required for humans to digest milk sugar. Almost everyone secretes abundant amounts of this enzyme in their youth. As humans mature many of them develop a deficiency in this enzyme subjecting them to nausea, cramping, pain and diarrhea. The over-the-counter medicine, LACTAID, provides an artificial source of this enzyme, so people who are so afflicted can comfortably eat pizza and Cherries Garcia ice cream.

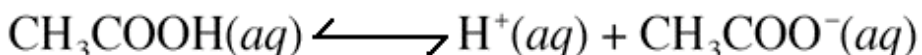
A much more serious enzyme deficiency is galactosemia. A key enzyme needed for the digestion of a fragment of lactose, called galactose, is missing in people who suffer from this malady. Because this enzyme acts within the human cell, the effects of its absence are much more severe and can include liver damage and mental retardation. The condition cannot be cured and the only solution is to exclude all milk products and any other food containing galactose from the diet.

Enzymes can also be inhibited by molecules or atoms, which insert themselves into the enzyme's "sweet spot" and prevent reactants from attaching where they should. Penicillin inhibits the enzymes in bacteria, which form the bacterial cell wall, thereby killing the bacteria.

- **Equilibrium**

Up to now we have spoken of chemical and physical processes as though they "go to completion": all the reactants disappear having been completely converted to products. In fact, this never happens in nature. At the end of a chemical reaction there is a mixture of product and reactant. In some cases, there is almost all product and reactant; in other cases very little product is formed.

A classic case of this is the ionization of a weak electrolyte:



In this equation, acetic acid ionizes in water to give hydrogen ions and acetate ions. In fact, in any solution of acetic acid, less than one per cent of the acetic acid is ionized. The sour taste (vinegar) means that there must be some H ions, but the weakness of the acid (we can put it on our potato salad, and live to tell about it) means that there aren't too many of them in solution.

We symbolize this situation with a new kind of reaction arrow, a double-ended arrow, indicating that there is evidence for the presence of significant amounts of both products and reactants at the end of the ionization process. We say that, in aqueous solution, acetic acid IS IN EQUILIBRIUM WITH hydrogen ions and acetate ions.

- **Idea of equilibrium**

If you are at a party and there are 100 other people there you may notice the following: as the evening goes on there are always a hundred people present but the identities of the people change. New people are constantly arriving, and others are leaving. The population at the party is said to be in dynamic equilibrium. If new people no longer show up, but those already there continue to leave, the party is no longer at equilibrium and eventually the population will decrease to zero.

If you place a glass of water on a window seal and leave it uncovered, all the water will evaporate. If you place a saucer over the glass however, the water won't dry up. Instead, water molecules will leave the liquid, bounce around, and return, much like the same guests being recycled through the same party again and again. The water and

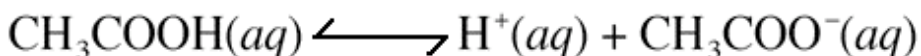
the entrapped water vapor above it are said to be in dynamic equilibrium.

We have equilibrium when the composition of some system stays the same indefinitely. We have dynamic equilibrium when the mechanism for this stability is the balancing of departure and arrival of one or more components of the system.

- **Expression for equilibrium constant**

Equilibrium Constant

Every process has its own, unique, set of equilibrium conditions. For chemical reactions, these will include some characteristic relationship between the amount of product and the amount of reactant. The quantity that sums this relationship up mathematically is called the equilibrium constant. For the ionization of acetic acid:



the equilibrium constant is given by the following equation:

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

The equilibrium constant, K_{eq} , is experimentally determined by measuring all the concentrations shown on the right hand side of the equation. Each chemical reaction has its own particular value for K_{eq} .

Equilibrium constants are often written with different subscripts to fit particular experimental situations or classes of compounds:

K_{eq}	the generic equilibrium constant
K_{c}	the equilibrium constant uses units of concentration
K_{p}	the equilibrium constant uses units of pressure
K_{a}	the equilibrium constant for a weak acid

K_b	the equilibrium constant for a weak base
K_{sp}	the solubility product for an ionic compound
K_d	the dissociation constant for a complex ion
K_w	the dissociation constant for water

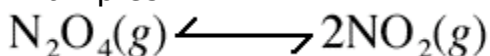
▪ **Writing it**

Writing K_{eq} .

Writing the equilibrium constant is fairly easy, you can infer this from a few easy rules:

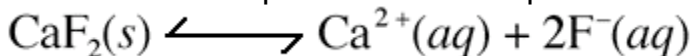
- The equilibrium constant is always a ratio of product concentration to reactant concentration.
 - Products are by convention the things on the right hand side of the chemical equation.
- Product concentrations are always raised to the power given by the stoichiometric coefficients.
- By convention, the concentration of one is assigned to water for aqueous solutions.
- By convention a concentration of one is assigned to solids.

Examples:



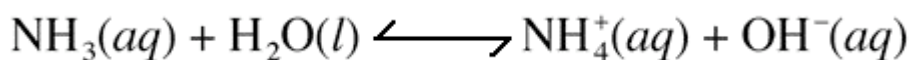
$$K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Note how the stoichiometric coefficient in the chemical equation becomes the exponent in the expression for the equilibrium constant.



$$K_{eq} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Note how the concentration of the solid is taken as one.



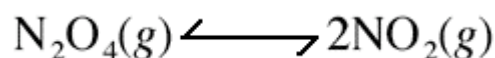
$$K_{\text{eq}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Note how the concentration of the water is taken as one.

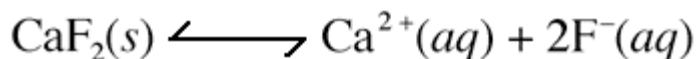
- **Units**

Equilibrium constants can have units. The units will depend on the stoichiometry and of course, on the units (usually Molarity) used to express concentration.

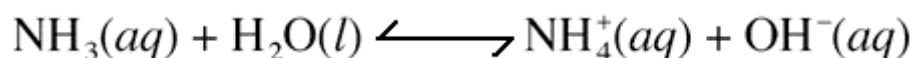
Reactions and Equilibrium Constant



$$K_{\text{eq}} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

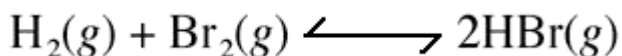


$$K_{\text{eq}} = [\text{Ca}^{2+}][\text{F}^-]^2$$



$$K_{\text{eq}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Sometimes the equilibrium constant can be dimensionless, for example:

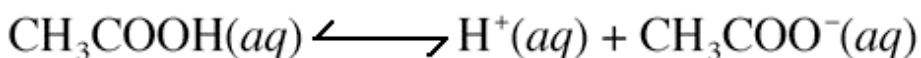


$$K_{\text{eq}} = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]}$$

- **Interpretation of expression for K_{eq}**

Meaning of K_{eq}

The equilibrium constant is a particular case of a much more general variable, the reaction quotient. We know the expression for the ionization of acetic acid and its equilibrium constant:



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

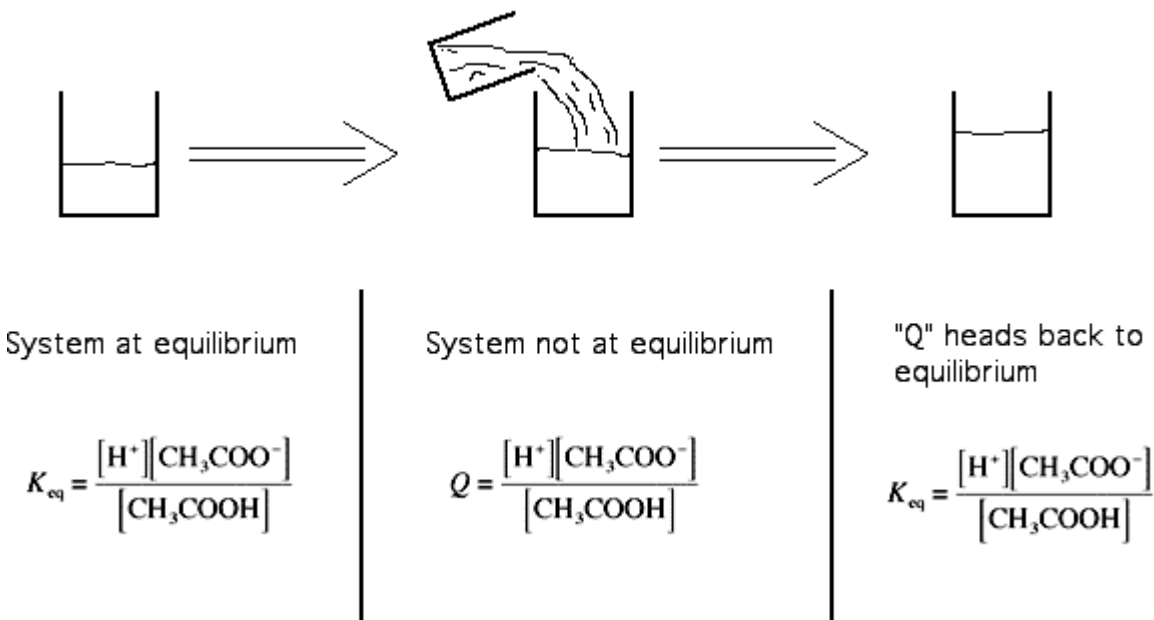
But how long does it take this process to come to equilibrium? When you make up a dilute solution of acetic acid, you add pure acetic acid to water. There has got to be some time lag, however short, between the point that you add pure undissociated acetic acid to water, and the

point where the acetic acid, the hydrogen ions and the acetate ions have achieved their equilibrium concentrations.

The point is that an equilibrium mixture is the *end* of a process; the process can start almost anywhere: how much water and how much acetic acid you start with is under your control: how much acetic acid, acetate ion, and hydrogen ion you end up with is under nature's control. The reaction quotient, Q , for the acetic acid equilibrium is defined as follows:

$$Q = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

This looks just like the expression for K_{eq} . In fact it is. K_{eq} is the special case of Q for when the reaction is at equilibrium. If you change any of the concentrations away from their equilibrium values, then the system is no longer at equilibrium and Q is the right letter to use. The system will then change by itself until the ratios of the concentrations yield the value of K_{eq} again:



The point is, that Q always tries to be K_{eq} . If you do anything to move a system away from chemical equilibrium, the system will try to return to equilibrium.

▪ Le Chatelier's Principle

The general idea that a chemical system, when moved away from equilibrium, will automatically adjust itself so that it returns to equilibrium is known as Le Chatelier's principle. A more formal statement of Le Chatelier's principle is as follows:

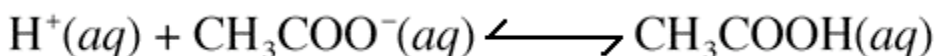
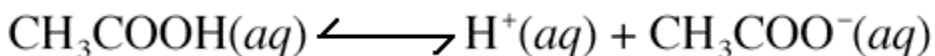
If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

We have just seen one aspect of the operation of Le Chatelier's principle in our discussion on the previous page of the mathematical meaning of the equilibrium constant. A disturbance in "the concentration of one of the components" of a system really means replacing K_{eq} with Q . The system "shift(ing) its equilibrium position so as to counteract the effect of the disturbance" corresponds to the return of the system to a state where Q becomes its special case value of K_{eq} .

Because product and reactant concentrations appear in the expression for Q , it is not surprising that they dictate, in some way, the position of equilibrium. Because, for a gas phase reaction, pressure is proportional to concentration, it is reasonable to expect that pressure may also influence equilibrium. Because heat can be a product (exothermic reaction) or a reactant (endothermic reaction), temperature will also play a role in equilibrium behavior.

General Considerations

In order to understand equilibrium arguments you must keep in mind a few simple "rules of the road". An equilibrium equation can be written in either direction:



Although we usually use the first equation, the second one says the same thing. In equation one acetic acid is the reactant; in equation two it is the product. The convention is that the left hand side of the

equation is always "the reactants" and the right hand side is always "the products".

When we say "the equilibrium is shifted to the left", we mean that the equilibrium concentrations have been altered in a way that more reactants have been formed. Likewise "shifted to the right" means shifted in the direction of the products.

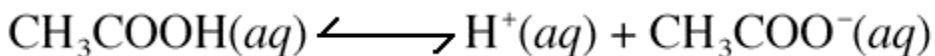
As noted above we usually write the dissociation of a weak acid with the aqueous ions as products. But we don't have to. The direction in which we write an equation is generally arbitrary. Once we have written it down, however, we must employ the terms product and reactant in a consistent fashion, as outlined above.

- **Dependence of equilibrium on:**
 - **Product concentration**

Effect of Product Concentration

Adding products to a reaction in equilibrium will shift the equilibrium to the left, resulting in the formation of additional reactant. Likewise, removal of product shifts the reaction to the right, resulting in the formation of additional product.

Consider the ionization of acetic acid:



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

If a strong acid is added to an equilibrium mixture of acetic acid, hydrogen ions and acetate ions, more acetic acid will be formed. This will also happen if a salt containing the acetate ion, such as sodium acetate, is added. In the latter case the pH of the solution will decrease, graphically demonstrating the equilibrium shift to the left.

Note how the expression for K_{eq} predicts this as well. Adding acetate ion is like adding stuff to the numerator. The only way the equilibrium constant can remain a constant, is for stuff from the numerator (products) to disappear and "move" to the denominator (reactants). The remarkable thing is that nature is smart enough to obey simple equations like these.

- **Reactant concentration**

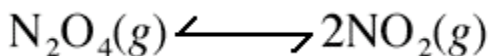
Effect of Reactant Concentration

Adding more reactant promotes the formation of additional products, whereas removal of reactant leads to additional reactant being formed from product molecules. Put another way, the addition of reactant shifts the equilibrium to the right, while the removal of reactant pulls the equilibrium towards the left.

The rationalization for this behavior in terms of K_{eq} is precisely analogous to that given for the case of product concentration on the previous page.

- **Pressure**

The best place to start to understand the effect of pressure on equilibrium is to look at an example:



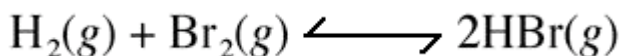
$$K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

From the stand point of Le Chatelier's principle, the most important thing about this equation is that there are more molecules on the right side of the equation than on the left. From the ideal gas law we understand that two moles of gas take up twice the volume as one mole of gas if all other conditions are the same. If you compress those NO₂ molecules, they can "wriggle out" of the situation by combining together to form a single molecule. Put in a different way, if you compress the NO₂ you have applied a stress to the system. The system can relieve this stress by assuming a configuration that takes up less room.

Thus, compressing the components of a gas phase reaction will always shift the reaction in the direction of fewer moles of gas, while decompressing such a mixture drives a reaction in the direction of greater number of moles.

Note that this is reflected in the expression for the equilibrium constant. Decreasing the volume by a factor of two increases the denominator by a factor of two but increases the numerator ([NO₂]²) by a factor of four (2²=4). To keep K_{eq} constant, material must "move" from the numerator to the denominator, from product to reactant, from the side containing more moles, to that containing fewer.

What about this reaction?



$$K_{\text{eq}} = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]}$$

There are equal numbers of moles on both sides of this equation and therefore compression has no effect on equilibrium. This is reflected in the fact that K_{eq} is dimensionless.

One final note: the pressure effects we are talking about arise from a physical compression of the reaction mixture and not from adding a gas that does not take part in the reaction. For example, if we added 100 atm's of argon to the NO₂/N₂O₄ mixture above, there would be no alteration in the equilibrium concentrations.

▪ Temperature

In an exothermic reaction, heat is a product. If you "add heat" to such a reaction (raise the temperature), the equilibrium will be shifted to the left (reactants). Likewise, if you cool the reaction, the products side will be favored. A completely symmetrical effect takes place in the case of an endothermic reaction.

Changing the position of equilibrium is not the same as changing the rate. Raising the temperature always increases the speed of the reaction (i.e., how fast it reestablishes equilibrium), but the effect of raising the temperature on the position of equilibrium will depend on whether the reaction is exothermic or endothermic.

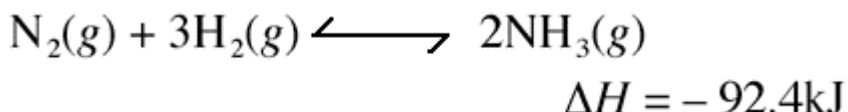
Note: when you change the temperature, you are actually altering the value of K_{eq} , something you are not doing when you change pressure or composition.

○ Example Haber process

The Haber Process

In world war one, Germany was blockaded by the British Navy and could not import nitrates for fertilizer and gunpowder. Just before the start of the war, Fritz Haber invented a process for manufacturing ammonia from nitrogen and hydrogen gas. Since ammonia can be easily transformed into nitrates, this process, the Haber process, enabled Germany to successfully withstand the blockade and prolong the war.

The process summarized by the following equation was based on a firm understanding of principle of chemical equilibrium.



For the Haber process to work well, everything possible must be done to drive the reaction to the right. Compressing the mixture works because there are fewer moles on the right hand side of the equation than on the left hand side. Removing the ammonia (by liquefaction) also drives the reaction towards the products.

Because the reaction is exothermic, cooling the vessel should also drag the reaction to the right. In fact it does...but at the cost of a dramatic reduction in reaction rate...once again the distinction between **position of equilibrium** and **rate at which equilibrium is approached** arises. For a process to work in the real world you can't sit around for a year waiting for the reaction to happen, no matter how good the product yield is. So Haber had to find a catalyst so that the reaction could proceed fast enough at relatively low temperatures.

Remember the catalyst lowered the activation energy, but it had no effect on the position of equilibrium. Keeping the temperature low for an exothermic reaction pushed the equilibrium to the right.

- **Difference between equilibrium and rate**

Rate versus Equilibrium

The Haber process illustrates the crucial difference between kinetics and equilibrium. Equilibrium concerns itself with how much of everything is there when the reaction ends, while kinetics asks, "how fast do we get there".

In the Haber process, lowering the temperature very much favors production of the desired product, ammonia. But the same strategy that drives the reaction to the ammonia side of the equation slows it down unacceptably. So a compromise must be reached: lower the temperature, but not too much, and add a catalyst to keep things moving along.

Even though kinetics and equilibrium reveal different aspects of a chemical reaction, they are related, and the course concludes with a brief discussion of this relationship.

- **Idea of dynamic equilibrium**

Dynamic Equilibrium

We introduced the topic of dynamic equilibrium using the analogy of a party in which the guests arrived and left in a steady stream, but the number of people in the living room stayed constant. There are many other analogies which come to mind: the number of cars in the peace bridge plaza might remain at one hundred for several hours, because the rate at which cars are passed through customs is precisely balanced by the rate at which cars arrive from the various feeder highways.

Any process in which some steady state is maintained by a constant and balanced inflow and outflow of material, heat, people...you name it...is an example of dynamic equilibrium.

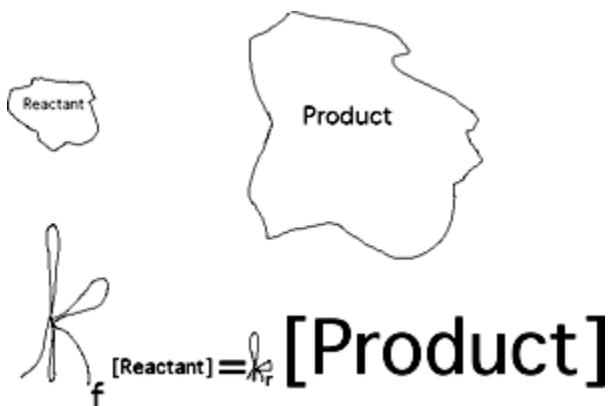
In a chemical reaction, reactants are always combining to form products, and products are always combining to form reactants. The reaction mixture is at equilibrium when the rate at which the products are formed from reactants is precisely balanced by the rate at which products are turned back into reactants. This is clearly an instance of dynamic equilibrium.

- **Relationship of equilibrium to rate**

Interdependence of Equilibrium and Rate

Remember that the rate equals the rate constant times the concentration to some power. This means that the rate depends on something intrinsic to the reaction (the rate constant), as well as the amount of reactant that is present. The bigger the rate constant, the faster the reaction: the greater the concentration of the reactant, the faster the reaction.

In any equilibrium situation, you have two competing reactions: the forward reaction and the reverse reaction. If the rate constant for the forward reaction is bigger than the rate constant for the reverse reaction, you will need a lot more product for the forward rate and the reverse rate to balance. Perhaps a picture would help:



If k_f is much bigger than k_r , the rates won't balance unless [products] is much bigger than [reactants]. Dynamic equilibrium requires that the rates balance. So if at equilibrium, the products predominate, this implies that the forward rate constant is much bigger than the reverse rate constant. Likewise, if reactants predominate at equilibrium, the rate constant for the reverse reaction is bigger. In fact the relationship between equilibrium and rate can be expressed mathematically:

$$K_{\text{eq}} = \frac{K_f}{K_r}$$