

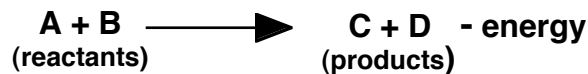
CHEMICAL REACTIONS *

Note: This is the first of a two-part set of notes. This set will review chemical reactions and the next will overview enzymes. What you learn in these two sections will be useful when you try to understand how other proteins such as receptors, channel and transport proteins, and antibodies function. The second set will consider biological catalysts – enzymes and ribozymes.

At their heart, organisms are complex chemical engines. However, many of the chemical reactions that organisms rely upon, although thermodynamically spontaneous (see review below), simply would not occur at an appreciable rate under the temperature and pressure conditions of cells. Other reactions are decidedly not spontaneous and will only proceed if coupled to reactions that are sufficiently spontaneous. Thus, specialized catalysts and coupling agents are required if reactions in the body are to occur at a rate commensurate with living processes. In most cases the role of catalyst/coupling agent is played by a special class of proteins, the enzymes. Enzymes are by far the most numerous catalysts in the body¹. Our bodies probably contain over 10,000 different types (perhaps many more) and most of these are responsible for catalyzing unique chemical reactions. A further appreciation of the importance of enzymes lies in the fact that most reactions occur in the body at rates somewhere between 10^7 and 10^8 times faster than they would without enzymes. Thus, the high levels of chemically-based process seen in organisms are the result of enzyme function. Finally, the organization and regulation of chemical processes, that is so much of a feature of life, is largely controlled (in the short term) by enzymes.

Uncatalyzed Reactions --- A Review

Let's say chemical species A and B react² under some conditions and release products C and D. Furthermore, the reaction releases a certain amount of energy (called free energy) in the process. We can write the reaction as:



reaction 1

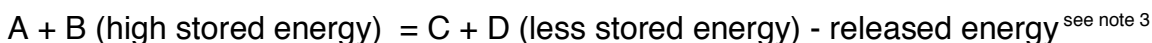
Notice that we follow the convention that whatever chemicals appear on the left side of the equation are designated as **reactants** and those on the right are called **products**.

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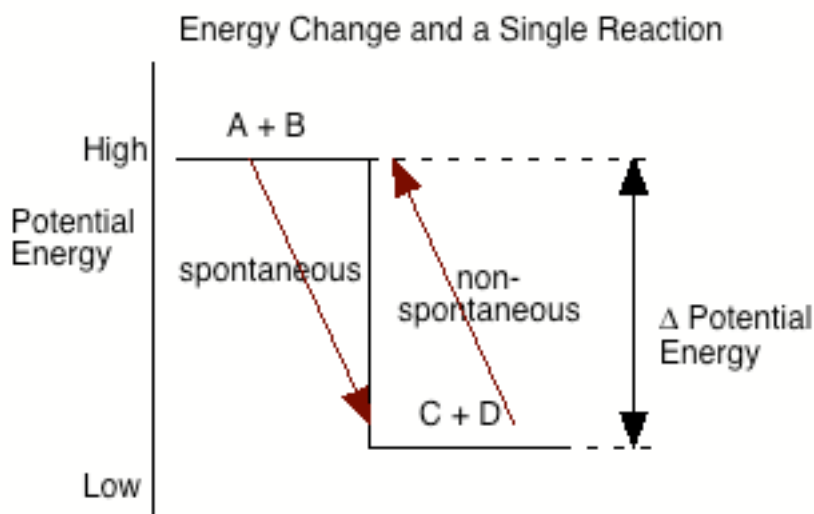
¹ There are other catalysts in the body, most notably certain types of RNA act as catalysts called **ribozymes**. However, ribozymes are not nearly as diverse as enzymes. More about these later.

² There is no particular reason why two reactants give two products. I could just as easily have had this discussion as $A \rightarrow B$ or $A + C \rightarrow D$ or whatever.

The reaction on the last page, like most reactions, has energy consequences. It resulted in a release of energy; such releases are conventionally designated with a **negative sign**. This released energy (sometimes called kinetic energy, but this can be a bit misleading) is the difference between the amount of energy that was contained in the reactants as compared to the products:



In this case the **reaction has done work on the surroundings** (by adding energy to the surroundings). We can view it graphically as:

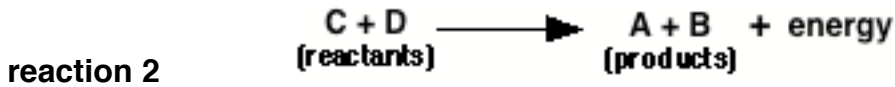


Notice that the total energy present in A and B and their surroundings before the reaction (the potential energy in reactants A and B) is still equal to the total amount of energy after the reaction. This equality is in accordance with the first law of thermodynamics -- energy is neither created nor destroyed.

A final note about reaction #1 -- the products C and D also contain some potential energy. But relative to the products, they contain less and can be thought of as no longer containing potential energy. On the other hand, if we reacted tC and D with something else, we may well see more energy released.

³ This released energy is often, somewhat misleadingly called "**kinetic energy**". Kinetic energy is recoverable the energy stored in the motion of objects and is equal to $1/2 mv^2$ (where m = mass and v = velocity). The energy released by the reaction may cause motion of matter whether that be heat or bulk motion. However, the energy could assume many other manifestations. For instance, the released energy could be in the form of light -- photons that are massless. So, unless you are specifically talking about kinetic energy, please think in terms of energy release -- in some form or another. The justification for using kinetic energy is historical (people were originally interested in the mechanical work that could be done by a process) and also related to the fact that all energy can be converted into heat which is at its heart a form of kinetic energy.

Reverse Reactions: We could also write reaction #1 in reverse:

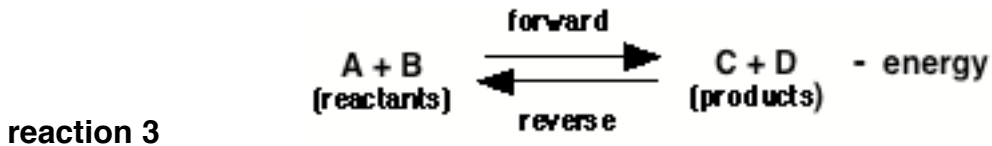


Notice that for this reaction to work, **it must absorb an amount of energy equal to that which is released in reaction #1**. We say that reaction #2 is **endergonic** since it absorbs energy from its surroundings. Put another way (that you should know), in this case the **surroundings do work on the reactants**.

The equations for reactions 1 and 2 encapsulate the notion that every chemical reaction is in principle "reversible". For example, given the correct conditions, either reaction 1 or 2 could proceed. Thus, we can write any process involving two states of matter and energy as the combined forward and reverse reactions (or processes). The two states in our example are:

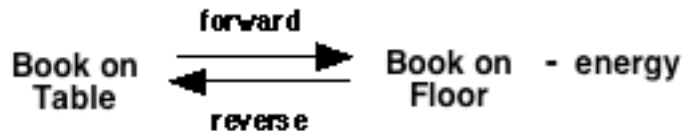
- A + B with lots of stored energy vs.
- C + D with less stored energy and more "kinetic" energy.

Thus:



This notion will lead us straight to our next topic, equilibrium.

About writing changes: Note that I could write just about anything with the forward <-> reverse notion shown above. For instance, imagine a book falling from a table to the floor. In the process energy stored in the book is released. To put the book back up on the table, I would need to utilize energy. Thus:



I can write any reversible process using this type of notion -- chemical reactions are not special in this regard.

What is the analog between the book on the table and the chemical equation above?

Where is the stored energy in these two examples?

(continued from last page)

What is the ground state in the book example? Is it the ground state for all times and conditions or only for this particular process? Explain.

Think of at least one other example from your own experience that can be written in the form above.

Chemical Equilibrium: The discussion above was best viewed as dealing with a single reaction (forward or reverse) at a time. For our purposes, there are two possible states: A + B (before the reaction) or C + D – free energy ("after the reaction"). There is no in between (or at least, it does not concern us) in this particular description. When we view a single reaction, we often say that we are working on the **micro** level.

However, there is another, very different, viewpoint that we can say is at the **macro** or "**population**" level. Here, we consider the overall or "system" behaviors of huge numbers of reactants and product atoms and molecules. Using a macro view, we don't talk about individual reactions so much as the total amounts of matter and energy involved in the reaction and the rates of reaction. So, a micro view of a reaction shows one of two possible states: A and B are or C and D. It is one or the other (ignoring so-called transitional states). By contrast, a macro view of a reaction involves looking at the proportions of the total that are either A, B, C or D (or "reactant" and "product"). One well-defined macrostate is called **equilibrium**. We will consider it in just a moment.

However, first let's consider the differences between amounts and rates. Amount is an easily mastered concept. Amounts in chemistry are measured in units such as mols when it comes to matter and joules or calories when it comes to energy. **Rates**, especially when applied to things like reactions, are a less familiar concept. With chemical reactions, rates are usually described as the **amount of a product that appears or reactant that disappears per time** -- thus, rates have units of **mols/time**. Alternately, they can be described **in terms of power** -- the rate of energy release or absorption in units such as **watts** (joules/s) or calories/time. Notice that this is based on the idea that fixed amounts of energy are released each time a single reaction occurs; the sum of all the energy over time is therefore a measure of the rate the reaction is moving in one direction or another.

The most useful way to express an organism's metabolism – that is, the sum total of all chemical reactions in its body -- is in energy per time. You will measure metabolism of humans and some other animals in lab.

When we have lots of product and reactant molecules together, we can describe a **forward reaction rate** and a **reverse reaction rate**. The difference between these rates is the **net rate of the reaction**. It is important to realize that in many cases both the forward and reverse rates will be very, very low -- near zero; under this circumstance, the net rate is also zero.

Let's now consider the concept of chemical equilibrium. We stated above that it is a well-defined macrostate, It is particular mix of products and reactants for a given reaction under a given set of conditions. At equilibrium the **forward and reverse reaction rates, averaged over a reasonable time scale, must**

be equal (they could both be zero or some finite value). Again, the result is no further change in macrostate.

Another way to look at equilibrium is in terms of energy. **The system** (all the entities under consideration -- example -- all reactant and product molecules and any "kinetic energy") undergoes no observable change on the macrolevel; moreover, they are incapable of undergoing any change on the macrolevel unless conditions are changed. There is no net change in the concentrations of reactants and products and there is not net change in "kinetic" or potential energy. Because there is not net change, such a system is no doing any work on its surroundings, nor are the surroundings doing any work on it. And since an equilibrium system is incapable of undergoing change on a macrolevel, it is incapable of doing or absorbing work. It is a condition of macro **stasis** -- constancy.

Everyone has played with a teeter-totter. Describe equilibrium conditions (how would the teeter totter need to be set up) for: both persons of equal weight, and where one person weighs 2X the other. Can the teeter/totter do useful work at equilibrium? How much energy does it possess?

On the other hand, even at equilibrium there may still be activity **at the microlevel**. The forward and reverse reactions may well be proceeding at some observable rate -- but, when averaged out (*i.e.*, when examined at the macro level) these **rates are equal**. Thus, although an individual reaction may occur that change reactants to products and release energy, another somewhere else will, sooner than later, convert some of the same type of products into reactants and absorb the energy that was released by the other reaction. On a macroscale, there is no net change.

The Equilibrium Constant, K_{eq} :

Whenever we start from some initial mix of chemical species⁴ we will find that there is some specific proportion of reactants and products that will be associated with equilibrium.

As you may recall, the equilibrium constant, K_{eq} , for a reaction is:

$$K_{eq} = \frac{\text{product of the concentration of the products each raised to their proportion}}{\text{product of the concentration of the reactants each raised to their proportion}}$$

Thus, for the forward reaction (reaction #1) we have been considering,

⁴ The value of the equilibrium constant **always** depends on proportions of different chemical species present before the reaction reached equilibrium; likewise, it depends on the **temperature** (for instance, for an exergonic reaction, it decreases with temperature).

$$K_{eq} = \frac{[C]^1 * [D]^1}{[A]^1 * [B]^1} \quad \text{-- at equilibrium}$$

Note that since C and D are designated the products and A and B the reactants and each species reacts in a proportion of 1:1:1:1.

Write an expression for the equilibrium constant for the reaction of acetic acid (CH₃COOH) with water to produce hydronium and acetate.

Now, what does this number, K_{eq} , mean? It is a number between zero (theoretically at least) and infinity (once again, theoretically at least). **If** its value is:

- = **1.0**, it means that at equilibrium there will be equal amounts of products and reactants. This is a very unusual situation but unfortunately, many seem to think this is what defines equilibrium (I guess because products and reactants are equal).
- < **1.0** -- at equilibrium, there will be more reactant than product -- the closer the value is to zero, the proportionately more reactant. One way to say this is that if K_{eq} is less than 1.0 the forward reaction is not favored.
- > **1.0** -- at equilibrium, there will be more product than reactant.

Do not make the common mistake of assuming that for a reaction to be at equilibrium, that there must be equal amounts of products and reactants. This is hardly ever true! Many reactions will reach equilibrium, the point of no further possible change (unless conditions change), with very little conversion of reactant to product (K_{eq} is between 0 and 1) or with very large conversions (K_{eq} is between 1 and infinity). For example, at equilibrium, nearly all ATP is converted to ADP and HPO₄²⁻ (phosphate or P_i); K_{eq} is very large for this reaction.

LeChartelier's Principle and Disequilibrium: When a system is at equilibrium, if it is disturbed by changing any of the reactants, products or energy, it will tend to minimize disturbance.. The system will return to an equilibril state (characterized in the last section) but this state will usually be somewhat different than the previous one -- *i.e.*, the new K_{eq} will not be exactly the same as the old. On the microlevel, one can explain LeChartelier by observing that providing excess C and D or energy (for instance) will cause some of the additional "stuff" to react. The reverse reaction speeds up relative to the forward reaction until some (but NOT ALL) of the "disturbance" is removed. Thus if additional C, D, or energy are added to our system (see rx #3) when it is at equilibrium, it will tend to convert some of these into A and B. Again, the result will be an approach (although usually not a perfect return) to the equilibril conditions given by K_{eq} . **Thus** disturbing a system that is at equilibrium will cause it to do some work **by**: rearranging chemical bonds and storing or releasing energy.

Hold onto to this idea as it will be very important when we consider reactions and work.

The Mass Action Ratio: We can write an equation that looks identical to that for K_{eq} for something called the **mass action ratio** or **q**. It differs in one very significant manner -- it is for any condition -- equilibrium or any number of an infinite number of states called disequilibria:

$$q = \frac{[C]^{1.0} * [D]^{1.0}}{[A]^{1.0} * [B]^{1.0}} \quad - - \text{any condition, including equilibrium}$$

We will **q** useful when we discuss the work that a reaction can do when not at equilibrium (remember when a reaction is at equilibrium, it can do no work).

Review and Thought Questions:

1. What should be the mathematical relationship between the K_{eq} for the forward and reverse reactions?
2. Will the same K_{eq} be obtained for both of these reactions? Explain.
eq. 1 $ADP + HPO_4^{2-} + \text{energy} \leftrightarrow ATP + H_2O$
eq. 2 $ADP + 2HPO_4^{2-} + \text{energy} \leftrightarrow ATP + H_2O + HPO_4^{2-}$
3. Assume that we start with the mixture given in eq. 1. When we reach equilibrium, there will be much, much more ADP and HPO_4^{2-} present than when we started and commensurately very little ATP. Before equilibrium which reaction (forward or reverse) was greater in rate? At equilibrium? Was work (in terms of energy) done on the system or by the system? How is equation 2 like disturbing system #1 by adding more HPO_4^{2-} ? Will there be more or less ADP at equilibrium in system #2? Explain. Describe what would happen to system #1 at equilibrium if more ADP or HPO_4^{2-} were added. More energy.

Reaction "Feasibility": The equilibrium constant predicts the equilibrium mix of products and reactants. It does NOT predict whether a reaction will occur nor does it predict the rate. K_{eq} is all about describing a particular static state. But what if we want to know whether or not a particular reaction CAN happen and moreover, what if we want to know something about WHETHER or not it will happen and HOW it will happen (steps and rates). To answer these two types of questions, we need to focus on approaches specifically referred to as:

- "Thermodynamics" (although it is a specific outgrowth the broader three laws of thermodynamics) which will tell us whether or not a given reaction will occur under a certain set of conditions and
- "Kinetics" which will tell us about the rate and mechanism(s) of the reaction.

Thermodynamics: This is the study of heat and its interactions with matter – especially in situations near equilibrium. Thermodynamics rests on three inductive generalizations known as the laws of thermodynamics. You probably remember that the first states that the total amount of energy and matter remains constant (conservation of energy/mass); the third has to do with a condition of no heat called absolute zero. We need to turn our attention, however, to the **Second Law of Thermodynamics**. It states that **in any spontaneous process the disorder or entropy of the UNIVERSE (i.e., the system and its entire surroundings) must increase.**

What is **disorder (entropy)**? It is a **measure the maximum number of possible positions or states of matter and energy**. If a gas expands into a larger volume, there is an increase in number of possible positions for each gas molecule -- thus, the gas system has experienced an increase in disorder (since there are more possible states). The opposite of entropy is order, where the number of states is highly constrained. **As entropy increases, we know less and less about the exact state or position of all of the matter and energy in a system; conversely, if disorder decreases, we know more and more about position and movement.** Thus, gases are inherently more disordered than solids; cold objects are more ordered than hot ones, big molecules more ordered than the same atoms in a number of smaller molecules. An **increase in entropy** that occurs as a result of some process such as a chemical reaction is written as a **positive value of ΔS** ; i.e.;

Eq. 1 $\Delta S = S_{\text{final state}} - S_{\text{initial state}}$

Thus, in mathematical terms, **a spontaneous process is one where $\Delta S > 0$** -- where entropy has increased. We have never observed anything that contradicts the second law.

But how do you measure changes in entropy for the entire universe? Is there an easier way to predict whether or not something is spontaneous? There is, it involves something called **Gibbs Free Energy** and that is our next topic.

Gibbs Free Energy and Spontaneous Chemical Reactions

When a process occurs, we have seen that the system undergoes a change in stored (internal) energy. When this process occurs at a constant pressure⁵, we call this change in internal energy the **change in enthalpy**, abbreviated as **ΔH** . By convention, whenever a system operating at constant pressure

- gains energy we assign the gain a positive sign.
- loses energy we assign a negative sign

⁵ Most chemical reactions in the body (and in solutions in general) occur under conditions of constant pressure. Other systems, such as gases, can easily be set up to achieve constant pressure.

Now, enthalpy (energy added to or removed from a system operating at constant pressure) can be seen as having two components.

Eq. 2. $H = \text{Energy Available for Useful Work} + \text{Energy Tied Up in Disorder}$

Let's consider the disorder term first. Disordered systems can be thought of as locking up a certain amount of energy in the disorder itself. One way to think about this is to imagine that increasing disorder means that molecules are freer to move about (there are more possible positions for the matter). The energy associated with this increased movement has been tied up and is essentially part of the disorder of the system. Mathematically the amount of energy tied up in disorder is given by the expression $T\Delta S$. Here, T is the absolute temperature in kelvins and ΔS is a measure of the change in entropy of the system (see eq. 1). Thus, as temperature increases more energy is tied up in the random motion of molecules. Likewise anything that increases disorder independent of temperature is measured by the term ΔS . For example, if a molecule breaks into several pieces or if energy is released and flows away, more disorder is produced and entropy increases (ΔS becomes more positive – see eq. 1).

The remaining energy, which is not tied up in disorder, can potentially be used to do useful work. We call this **Gibbs free energy** and symbolize the amount that it changes as the result of a process as ΔG . Thus, we can re-write and re-arrange eq. 2 to give what is known as the Gibbs free energy equation:

Eq. 3. $\Delta G = \Delta H - T\Delta S$

-- in other words, the Gibbs free energy change is the difference between the total enthalpy change in some process and the change in energy tied up in disorder.

So what good is all of this? It is a bit beyond our course to explain why, but knowledge of ΔG will allow us to predict whether or not a reaction is **spontaneous**. Recall that earlier we said that a process is spontaneous if the disorder of the universe increases. It is not easy to measure the change in disorder for the entire universe. With Gibbs free energy, we need only know about the isolated system in order to predict if the process is spontaneous. In fact, we can make the following rules (which you should know):

- $\Delta G < 0$ (*i.e.*, is **negative**) -- the process is currently not at equilibrium and is **spontaneous** in the direction written
- $\Delta G = 0$ -- the process is currently **at equilibrium**
- $\Delta G > 0$ (*i.e.*, is **positive**) -- the process as written is not at equilibrium and will require an energy input to move in the forward direction. We say it is **non-spontaneous**.

You have seen many spontaneous processes that involved releases of heat. Setting something on fire or dissolving most strong acids in water are great examples of processes that are both spontaneous and that involve large negative ΔH values. *This leads to the erroneous belief in many people that spontaneous processes must release heat.* But there are many examples of spontaneous processes that absorb heat. If this were not the case, the cold packs used in first aid would not exist. In this case, starting the reaction (by mixing the components in the protective pouch) sets off a reaction that absorbs heat -- instant cold! Likewise, there are processes with negative ΔH values that are NOT spontaneous.

If we consider the Gibbs free energy equation, it should now be easy to see how a system with a positive enthalpy could still be spontaneous. If such a system absorbed energy ($+\Delta H$) but at the same time disorder increased sufficiently, thereby giving a large ΔS (for example by atoms dissolving into a liquid – something that happens in a cold pack) then the overall free energy change would still be negative and the process would be spontaneous!

Important note: Gibbs free energy **will not predict the rate the reaction or when it will occur.** So, the oxidation of glucose to water and CO_2 by oxygen is highly spontaneous (a very negative ΔG) yet it proceeds at a rate of essentially zero under conditions in your sugar bowl. To study rate, we need to get on with **kinetics**.

? What do $\Delta G = +1$ and K_{eq} of 1.0 mean?

If the forward reaction has a positive ΔG value, what sign does the reverse reaction have? Explain.

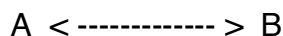
Be sure you know the formula for Gibbs free energy and can interpret the meaning of different values of this parameter.

Different Values of Gibbs Free Energy for the Same Reaction: ΔG is a system (population) property -- it is not a property of a single reaction of (for instance) A and B to make C and D. The free energy of a system always depends on how far it is displaced from its equilibrial (most disordered) state. This is because any system not at equilibrium can react in some direction and reach equilibrium. Accordingly, there must be free energy consequences when any system is displaced from K_{eq} . Recall that we said earlier that we could use a mathematical expression called the mass-action ratio (q) to describe the system for any set of concentrations. Chemists have discovered that the amount of Gibbs free energy in any system can be calculated from the following expression:

$$\text{Eq. 4 } \Delta G = - RT \ln \frac{K_{\text{eq}}}{q}$$

where R is the gas constant and T is the absolute temperature and **ln** means "the natural log of".

Let's not memorize this equation but instead let's look and see if it makes sense. Consider the simple reaction



- Where for the forward reaction $K_{\text{eq}} = 2$. Thus, at equilibrium, B will be at twice the concentration of A. However, let's say we have a mix of products and reactants such that $q = 0.5$
- This means that there is a greater proportion of reactants than is predicted for equilibrium.
- Thus, the system should be able to do work.
- According to LeChartelier, in this case the forward reaction should increase until a new equilibrium was reached.
- Whenever we have the potential for a net forward reaction, (i.e., the forward reaction is feasible) then ΔG **must be negative**.

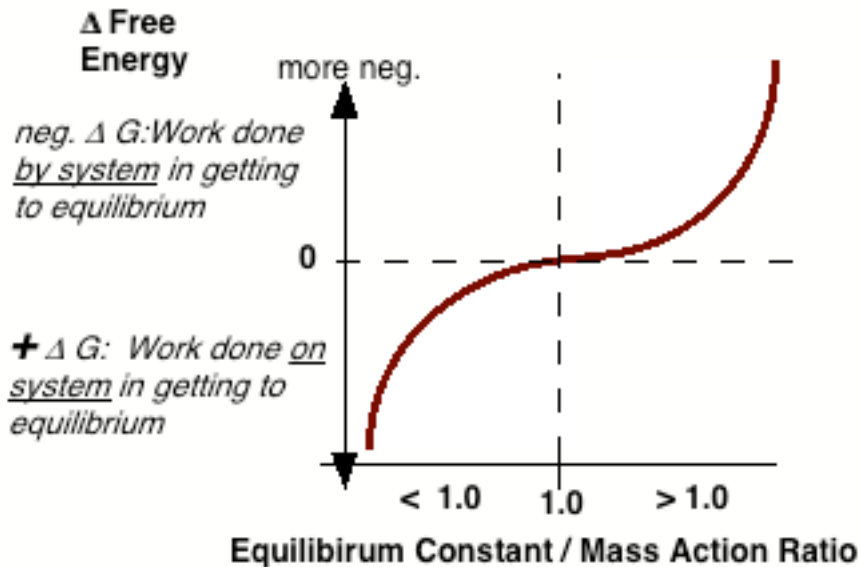
Thus, $K_{\text{eq}} / q = 2 / 0.5 = 4$. The log of a number greater than 1 is always positive. So, in this case, ΔG is negative (see the equation to see how I got a negative) and the forward reaction is spontaneous.

Go back and review logarithms -- be sure you know that the sign of logarithms greater and less 1.0 (and therefore the ln or log of 1).

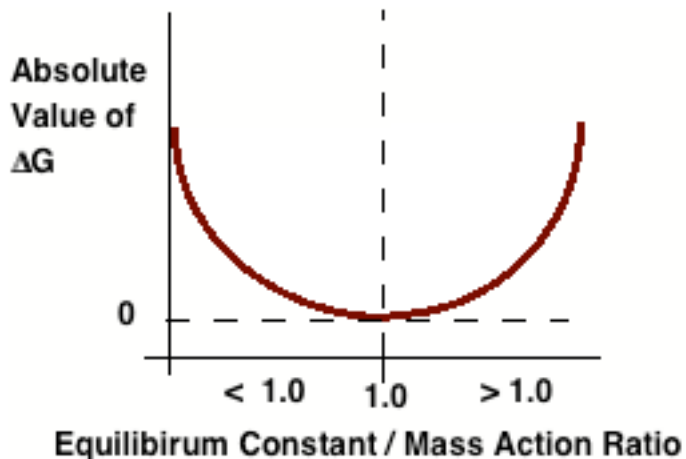
Be sure you can do these next problems:

What would be the case if q had been 10? Are there "too many" products or reactants? Which way should the reaction go to get to equilibrium? Should ΔG be positive or negative? Check!

Here is a graphical depiction of what we have just talked about:



An alternative view that better illustrates the idea of equilibrium is where we plot the **absolute value of the free energy change** on the Y-axis:



Notice first that we are simply looking at the absolute value of the free energy of the system -- work can be done anytime we displace from equilibrium and the further the displacement, the more work that can be done.

To displace a system from equilibrium, does work need to be done? Can that work be recovered? Could the graph above also be viewed as telling you how much stored energy there is in a system?

Standard Gibbs Free Energy Changes: Hopefully the discussion above shows you that the conditions and the reaction determine the free energy change. Obviously for every reaction, there are an infinite number of possible conditions.

To compare the general energy characteristics of reactions, we need a standard set of conditions. In biology, these generally mean the following:

- 1 atmosphere pressure
- constant volume
- Temperature = 298 kelvins
- pH = 7.0
- concentrations of all products and reactants = 1.0 Molal

When the free energy is found for a particular reaction at these conditions, it is called the **standard free energy, ΔG°** .

Obviously, these conditions are usually nowhere near equilibrium and for different reactions they are more or less displaced. Moreover, they are nothing like typical conditions in a cell.

ΔG° values can be very useful in comparisons. Most free energy changes you see listed in textbooks (for instance the famous -7.3 kcal for the breakdown of ATP to ADP and HPO_4^{2-}) are standard free energy changes. They are great for comparisons. However, they must be looked at skeptically because they often tell nothing about the reaction in cells. For instance, it is quite common for reactions to have positive ΔG° values but to have negative ΔG values in actual cellular conditions. Reactions that will not "go" in the lab under standard conditions often work just fine under different conditions in cells. Alternately, as with ATP, reactions with a certain negative standard free energy changes have much more negative changes in the cell.

The more negative the ΔG , what about the amount of chemical work done in going to equilibrium?

Kinetics: Thermodynamics predicts whether or not a reaction is feasible (possible) and it tells us the extent to which the reaction will proceed (*i.e.*, how much of the reactant will be converted to product with how big of an energy change). On the other hand, thermodynamic considerations never tell us:

- the rate of the reaction
- the mechanism or path of the reaction -- how A and B turn into C and D

We will ignore the second for the moment. Let's consider rate.

Just because a reaction is spontaneous does not mean that it will proceed at a measurable rate. Take sugar in an opened bowl in your room. The sugar is surrounded by highly reactive oxygen gas. The reaction between sucrose and oxygen is highly spontaneous:



Notice the large, negative ΔG , indicative of a spontaneous forward reaction. At completion, nearly all of the sugar will have reacted with oxygen to give CO_2 and

water. Yet, you know from personal experience that sugar bowls, when uncovered, do not spontaneously burst into flames. Why is this? After all, the forward reaction is far from equilibrium and is very spontaneous, thermodynamically speaking.

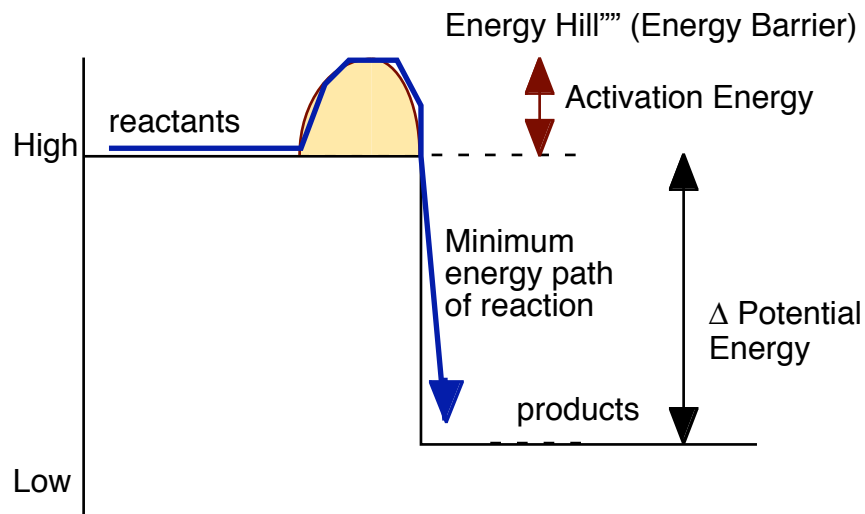
The reason is that in order for oxygen and sucrose to react, the following things must happen:

1. The bonds in the sugar molecule must be "stressed" sufficiently so that that they can interact with oxygen. One way to think about this is that the distances and angles between the atoms in the bonds of sugar need to be altered (for example, by lengthening)
2. O₂ and sucrose molecules must collide with sufficient energy.
3. The collision must be sterically correct -- *i.e.*, the O₂ and sugar molecules must have the correct orientation with respect to each other in order to react.

In the case of our sugar bowl, items 2 and 3 are certainly occurring but condition #1 is not true -- at least at room temperature. Now, what if you put the sugar in a microwave or in a frying pan (or, in a closed chamber with oxygen at extremely high pressures and maybe a little heated to boot?). The result will be similar in all cases -- the sugar will begin to react and we will see it burn either slowly or actually burst into flames or explode. What happened? In the case of the microwave, the sugar molecules absorb some of the energy. This causes them to begin wiggling around more -- atoms literally swing back and forth (vibrate) along their bonds. In the case of the frying pan, something very similar happens except this time the source of the motion was the heat of the pan itself. In the last case, the greater amounts of warm oxygen increased the number of collisions between oxygen and sugar. Moreover, the collisions transferred energy to the sugar (as with the frying pan) and caused more bond distortion.

What we have seen is that we often need to add certain amount of energy to provide the correct conditions (items 1 to 3 on the last page) for a reaction to occur. This is called **activation energy** or E_A . The amount that will be needed depends on the reaction itself and the physical conditions surrounding the reactants. Clearly more energy will need to be added to the sugar if the entire system is just above absolute zero as compared to if it is already at 250°C (just below where the reaction will start). Again, this energy strains the bonds so that at a greater percentage of the time they are in configuration where they can react and it increases the frequency of sterically correct collisions. So, the reaction rate goes up.

We often think of E_A as a type of barrier that must be overcome for a reaction to occur. You have certainly seen a diagram like the one on the next page:



Notice that the activation energy is not lost.

One final point about kinetics. Although we will not be greatly concerned with it in this course, kinetics is also about the prediction of the exact reaction mechanisms and path. In our example with sucrose, which is a large complex molecule, there are many ways to accomplish its breakdown to water and CO_2 . There are many possible sequences and to finally get to just 12 waters and 12 CO_2 molecules. Each represents a **separate reaction path**. In burning sucrose by heating it, we do not control the reaction path. The result in such uncatalyzed reactions is that many different paths are followed (some sucrose molecules are broken down one way, others in other ways). However, the final change in bound energy result is independent of the exact path -- by the time the sucrose is fully broken down, the same amount of energy is released regardless.