Lecture 33

So far in talking about thermodynamics, we've mostly limited ourselves to discussions of thermochemistry, a quantification of the heat absorbed or given off as the result of a chemical reaction. However, thermodynamics can do much more than this. It can help us with predictions about when products or reactants will be favored at equilibrium, whether reactions will occur spontaneously, and even predict the value of the equilibrium constant. It will also help us answer questions about whether, and to what extent, the equilibrium constant will change when we change the temperature or the pressure.

Chemical thermodynamics can answer these questions quantitatively. **Thermodynamics can tell us two things** that are extremely important in chemistry. **The first of these is which processes will occur spontaneously**, i.e., without doing work on the system. Whether a solution will form when two substances are mixed is one example of a question which thermodynamics can answer. **The second thing which thermodynamics tells us is what the conditions are for a system to be in equilibrium.** In this chapter, we will concentrate on understanding when a process will be spontaneous, i.e, will occur without doing work on the system, and practice calculations with some special functions of thermodynamics.

In order to predict the things that we want to know, **it is necessary to describe our system precisely**. In general, **this means knowing the temperature, pressure, and mole number of each of the components of the system**. These variables taken together are called the **state of the system**. For example, suppose I have a 5.00 mol sample of Ar(g) at 298K and 1.00 atmosphere pressure. This sample is in a different state than a 2.5 mol sample of Ar(*l*) at 30K and 4.00 atm pressure. **All the properties of the system will**

depend on the state of the system.

We also have some **names for the conditions under which we run our experiments**. An **isothermal process** is one in which we keep the temperature constant. An **isobaric** process is one in which the pressure is kept constant. Finally, if we run our experiment so that no heat can flow into or out of our system, then the processes that occur are called **adiabatic** processes.

All of the conclusions that we draw from thermodynamics are based on three laws. We dealt in some detail with the first law of thermodynamics in the first third of the semester. **The first law states simply that "The energy of the universe is constant"**. To reiterate, the importance of this law is that no process is possible if energy must be created or destroyed for it to occur. Thus the first law gives us a tool for energy "bookkeeping". This bookkeeping is easier because **energy is a state function**. This means that for any change in state, $\Delta E = E_{final} - E_{initial}$, independent of the path between the states. **Energy can be changed by doing work on a system, or by heating the system**.

Enthalpy and energy, to which it is related, are considered **first law quantities**, since they tell us about the way energy is absorbed or emitted when a chemical reaction occurs. Basically they tell us when a process is possible. For example, a process requiring energy will not occur unless we supply the necessary energy.

In this section we will concentrate on two other useful things which thermodynamics tells us, whether a process will be spontaneous, and whether the products or reactants will be favored in a system when it reaches equilibrium. The law of thermodynamics that governs the equilibrium composition and reaction spontaneity is the second law of thermodynamics. **The second law of thermodynamics consists of two**

statements - The entropy of the universe increases for a spontaneous process, and the entropy of the universe is unchanged for a reversible process.

Of course, neither statement makes sense unless we know what entropy is. **Entropy is simply a measure of the disorder or randomness in a system.** We can see that there is a tendency toward disorder in many everyday events. HOW MANY OF YOU HAVE PLAYED 52-CARD PICKUP? IF YOU TAKE A NEW DECK OF CARDS, WITH ALL THE CARDS IN ORDER AND THROW IT UP IN THE AIR, DOES IT COME BACK DOWN IN ORDER OR WITH THE CARDS MIXED? IF YOU START WITH THE DECK OUT OF ORDER AND THROW IT UP IN THE AIR, WILL IT EVER LAND IN ORDER? So you see there is a tendency for things to proceed naturally from a state of order to one of disorder. You can also see signs of the natural tendency toward disorder in the way that an abandoned building gradually decays. **Since disorder is a measure of entropy, the greater the disorder of a system, the greater the entropy of the system.**

Let's look at some systems of chemical interest to see which has greater disorder and therefore greater entropy. As the first case let's consider a solution vs. the solute and solvent that make up the solution. At first we have only solute next to solute and solvent next to solvent. When the solution is formed, the solute is dispersed throughout the solvent. WHICH IS MORE DISORDERED? Therefore the entropy of a solution is greater than the entropy of the separated solute and solvent. We symbolize the entropy as S.

Entropy is a state function, and therefore we can calculate the entropy change for any process by taking the difference between the initial and final entropies, i.e., $\Delta S = S_f - S_i$. For the process of solution, the change in entropy would be $\Delta S = S_{solution} - S_{solvent} - S_{solute}$. Since the entropy of the solution is higher, we can conclude that $\Delta S_{solution} >$

0.

Another example to consider would be the entropies of the solid, liquid and vapor phases of the same chemical. In the solid, each particle is assigned a fixed position, and everything is regularly spaced. In the liquid, there is a little more space between particles, and the particles can move around each other. WHICH IS MORE DISORDERED, THE SOLID OR THE LIQUID? THEREFORE, WHICH HAS THE HIGHER ENTROPY, THE SOLID OR THE LIQUID? Now let's consider the gas. In the gas, the particles have a great deal of space between them and can move around with almost complete freedom. WHICH HAS THE HIGHEST DEGREE OF DISORDER, A SOLID, LIQUID, OR GAS? WHICH HAS THE HIGHEST ENTROPY? Suppose we freeze a gas. The process can be written gas → solid. The entropy of freezing will be given by $\Delta S_{freezing} = S_{solid} - S_{gas}$. Since the entropy of the solid is less than the entropy of the gas we conclude that $\Delta S_{freezing} < 0$. WOULD $\Delta S_{VAPORIZATION}$ BE POSITIVE OR NEGATIVE?

Heating an object can affect the amount of disorder in the system. Remember that temperature is a measure of kinetic energy, the energy of motion. In other words, the higher the temperature of something is, the more its particles are moving. Let's figure out the effect of motion on disorder by considering the two extreme cases. In one case we'll consider a group of 9 particles which are not moving at all. Now consider a group of particles that are the same distance apart as the first group, but are whizzing around. Clearly, the group which is stationary is more ordered. Since the only difference between the two groups of particles is motion, we conclude that increasing motion increases entropy. Since heating a system increases the amount of motion, heating the system also increases the entropy. We symbolize this by saying $\Delta S_{heating} > 0$.

Let me ask you a question. WHICH HAS GREATER ENTROPY, WATER AT 350K OR WATER AT 300K?

Finally let's consider a couple of chemical reactions. First let's look at the reaction

$$H_2(g) \rightarrow 2\ H(g).$$

For simplicity let's look at just four H_2 molecules. At first all the hydrogens are combined and can only move in pairs. If we break the bonds of all four hydrogens, we now have eight hydrogen atoms, all of which can move by themselves. WHICH IS MORE DISORDERED? WHICH HAS GREATER ENTROPY? The entropy change for the reaction is $\Delta S_{rxn} = 2\ S_H - S_{H2}$. Since two H atoms have a greater entropy than one H_2, $\Delta S_{rxn} > 0$ for this reaction.

For another example consider the reaction, $N_2 + 2\ H_2 = N_2H_4$. Suppose we start out with 4 nitrogen molecules and eight hydrogen molecules. Before the reaction occurs all 12 particles can move freely around the container. If the reaction goes to completion, the twelve independent molecules combine to form only 4 hydrazine molecules. WHICH IS MORE DISORDERED THE REACTANTS OR THE PRODUCTS? WHICH HAS HIGHER ENTROPY? IS ΔS_{RXN} POSITIVE OR NEGATIVE FOR THIS REACTION? OUR GENERAL CONCLUSION IS THAT THE SIDE OF THE REACTION THAT HAS THE GREATER NUMBER OF PARTICLES WILL HAVE THE GREATER ENTROPY.

Lecture 34

In our discussion thus far, we have talked about the relation between disorder and spontaneity, defined the entropy as a measure of the disorder of a system, and done qualitative evaluations of the entropy of various systems. It would be useful if we could do quantitative calculations of entropy changes, especially for chemical reactions. For a chemical reaction, the entropy change is given by ΔS_{rxn} = S(all the products) - S(all the reactants). The easiest way to calculate the entropy of a reaction is if we know **S, the absolute entropy**, for each of our reactants and products.

In fact, **tables of absolute entropies** are commonly available. We can calculate these absolute entropies because of the third law of thermodynamics. The **third law of thermodynamics says "the entropy of a perfect crystal of a pure substance is 0 at 0K."** By a **perfect crystal** we mean one in which there are no gaps in the regular arrangement of atoms which make up the crystal. This law should make basic sense. First consider what happens to entropy as we go from gas to liquid to solid. Since the system gets more and more ordered as we move toward the solid, the entropy keeps decreasing. Now consider a solid at a given temperature. Remember that the lower the temperature is the lower the entropy is. Now if we have a solid at 0K, we have the lowest possible temperature and therefore the lowest possible entropy. It turns out that if we have a perfect crystal of a pure compound, then this lowest possible entropy is 0.

The result of this is that **by starting with pure crystals at 0K, we can figure out the entropy of any substance at any temperature. These entropies depend on external pressure, so to simplify things, they are tabulated at one standard pressure, one atm.** These one atmosphere entropies are called **Standard Entropies**, and are symbolized by

S°. As we've said before, **entropies also depend on temperature, so when we report a standard entropy, we must specify the temperature**. So for example, the standard entropy for hydrogen gas at 298K would be written as S^0_{298} (H_2(g)).

Just as we used standard heats of formation to calculate standard heats of reaction with the equation ΔH^0_{rxn} = ΔH_f°(products) - ΔH_f°(reactants), **we can use our absolute entropies to calculate entropies of reaction with ΔS_{rxn}° = S°(products) - S°(reactants)**. Let's practice on the two reactions we've already mentioned. For the reaction

$$H_2(g) \rightleftharpoons 2\ H(g),$$

our standard entropy of reaction at 298K will be

$$\Delta S_{rxn,298}° = 2 * S_{298}°(H(g)) - S_{298}°(H_2(g)).$$

If we look in a table of standard entropies, we find that S_{298}° for H_2(g) is 130.6 J/mol K, and S_{298}° for H(g) is 114.6 J/mol K. Therefore our entropy of reaction is $\Delta S_{rxn,298}$° = 2 * 114.6 - 130.6 = 98.6 J/mol K. The reason we use 2 times the entropy of the H atoms is that we are taking the difference of the total entropy of our products from the total entropy of our reactants. If we write our reaction as $H_2(g) \rightarrow H(g) + H(g)$ we see that the total entropy of the products is the entropy of 2 H atoms.

As a second example we'll calculate the entropy of the reaction

$$2\ H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l)$$

at 298 K. Our entropy will be given by

$$\Delta S_{298}° = S_{298}°(N_2H_4(l)) - S_{298}°(N_2(g)) - 2 * S_{298}°(H_2(g)).$$

We already know the standard entropy of H_2(g), and our table tells us that $S_{298}°(N_2H_4(l))$ = 121.2 J/ mol K and $S_{298}°(N_2)$ = 191.5 J/ mol K. Therefore the reaction entropy is

$$\Delta S_{rxn,298^{\circ}} = 121.2 - 2*130.6 - 191.5 = -331.5 \text{ J/ mol K.}$$

Do these entropy changes we've talked about correctly predict reaction spontaneity? Let’s make a list of some of our processes and the signs of their entropy changes. For the reaction $H_2(g) \rightarrow 2\ H(g)$, ΔS was positive. For $\Delta S_{vaporization}$, ΔS was positive, as was $\Delta S_{solution}$. However, we know that H_2 will form spontaneously from H atoms, that at low enough temperature condensation will be spontaneous, and that for some substances solutions will not form. Yet the second law says that the entropy of the universe increases for a spontaneous process. The answer to our problem lies in the word universe. Remember that the universe is system + surroundings, so that **when we say the entropy of the universe is increasing we write $\Delta S_{system} + \Delta S_{surroundings} > 0$ for a spontaneous process**. All of the entropies that we have calculated so far have been entropies of the system alone. In order to make a prediction about spontaneity we need to know what the entropy change of the surroundings is. This may sound daunting, but fortunately **for experiments done at constant temperature and pressure, the entropy of the surroundings is given by**

$$\Delta S_{surr} = -\Delta H_{system}/T_{system}.$$

This means that we can write our requirement **for spontaneity as $\Delta S_{system} - \Delta H_{system}/T_{system} > 0$**. This is really neat. Notice that **we have figured out how to find the entropy change of the universe by referring only to the system**, which we know a lot about, and without having to refer directly to the surroundings, which we know little about because they are so huge.

We usually get rid of the fraction in this equation for spontaneity to give the equation $\Delta H - T\Delta S < 0$ for a spontaneous process at constant T and p. Because this equation is so useful **we give the term ΔH - TΔS a special name, the Gibbs free energy, ΔG**. So we can now restate the second law as follows: **for a spontaneous process at constant temperature and pressure ΔG < 0**.

Consider the reaction $C_2H_4 \rightleftharpoons C_2H_2 + H_2$. **When ΔG < 0, it means that the reaction will spontaneously form more products**, acetylene and hydrogen. What is really neat is **if ΔG > 0, the opposite reaction, formation of ethylene, will be spontaneous**. Neatest of all, **if ΔG = 0, the forward and backward reactions balance each other out, and the reaction achieves a dynamic equilibrium**. This is so important that it bears repeating. For a reaction at constant pressure and temperature, if ΔG < 0, the reaction will spontaneously proceed toward products. If ΔG>0, the reaction will spontaneously proceed toward reactants. Finally if ΔG = 0, the system will be in equilibrium.

When we make a reaction mixture, ΔG depends on the concentrations of all of our reactants and products, i.e., **ΔG depends on concentration**. Since as the reaction proceeds the concentrations change, **ΔG changes as the reaction proceeds**. In general as a reaction proceeds, it approaches a state of dynamic equilibrium, so **ΔG tends to approach 0, as the reaction goes on**.

We define the standard free energy, **ΔG°, as the free energy difference which accompanies the conversion of reactants in their standard states to products in their standard states**. We can calculate these using **standard free energies of formation, ΔG°**, which are defined as **the free energy change when a mol of a substance is formed from its reactants in their reference states.** We usually can look up free energies of formation in tables. In addition, just as the heat of formation of elements in their stablest states is defined to be 0, **$\Delta G_f°$ of elements in their stablest states is defined to be 0**. For example, since hydrogen's stablest form at 298K is $H_2(g)$, $\Delta G_{f,298}°(H_2(g)) = 0$. WHAT IS THE FREE ENERGY OF FORMATION OF HG(L) AT 298K?

We calculate $\Delta G°$ of reaction with the rule

$$\boldsymbol{\Delta G_{rxn}° = \Delta G_f°(\text{products}) - \Delta G_f°(\text{reactants})}.$$

For example, for the reaction

$$2NH_3(g) + 7/2\ O_2(g) \rightleftharpoons 2NO_2(g) + 3\ H_2O(g),$$

$\Delta G_f°(NH_3(g)) = -16.64$ kJ/mol, $\Delta G_f°(NO_2(g)) = 51.84$ kJ/mol, and $\Delta G_f°(H_2O(g)) = -228.60$ kJ/mol. WHAT IS$\Delta G_F°(O_2(G))$? For this reaction,

$$\Delta G_{rxn}° = 2 \text{ x } \Delta G_f°(NO_2(g)) + 3 \text{ x } \Delta G_f°(H_2O(g)) -2 \text{ x } \Delta G_f°(NH_3(g))$$

$$= 2 \text{ x } (51.84) + 3 \text{ x } (-228.60) - 2 \text{ x } (-16.64) = -548.84 \text{ kJ/mol}.$$

When we introduced the Gibbs Free Energy, we defined it by $\Delta G = \Delta H - T\Delta S$. This equation is important because it tells us about reaction spontaneity and about chemical equilibrium. To reiterate, if we have a reaction like $N_2 + 3H_2 \rightleftharpoons 2NH_3$, and ΔG is < 0, the forward reaction, formation of ammonia, will occur spontaneously. If $\Delta G > 0$, the reverse reaction, decomposition of ammonia, will occur spontaneously. Finally, when $\Delta G = 0$, we will have an equilibrium between reactants and products.

Our definition of ΔG shows that we can calculate standard free energies from standard enthalpies, and standard entropies, i.e., at 298K,

$$\Delta G_{298}° = \Delta H_{298}° - T\Delta S_{298}°.$$

For example, for the reaction

$$C_2H_4 \rightleftharpoons C_2H_2 + H_2,$$

$$\Delta H_{rxn,298}° = \Delta H_{f,298}°(C_2H_2) + \Delta H_{f,298}°(H_2) - \Delta H_{f,298}°(C_2H_4).$$

Looking in any table of thermodynamic data, we find that the standard heats of formation at 298 of C_2H_4 and C_2H_2 are 52.26 kJ/mol and 226.73 kJ/mol respectively. DOES ANYONE REMEMBER WHAT THE STANDARD HEAT OF FORMATION OF H_2 IS? So

$$\Delta H_{rxn,298}° = 226.73 - 52.26 \text{ kJ/mol} = 174.47 \text{ kJ/mol}.$$

For this reaction

$$\Delta S_{rxn,298}° = S_{298}°(C_2H_2) + S_{298}°(H_2) - S_{298}°(C_2H_4).$$

HOW DO WE FIND ABSOLUTE ENTROPIES? When we look them up we find that they are 200.94, 130.684 and 219.56 J / mol K respectively and therefore

$$\Delta S_{rxn,298}° = 200.94 + 130.684 - 219.56 = 112.06 \text{ J / mol K}.$$

Now we calculate the standard free energy using $\Delta G_{298}° = \Delta H_{298}° - T\Delta S_{298}°$. The only thing that we have to watch out for is making sure that all the units are the same, since enthalpy is in terms of kJ and entropy in terms of J. Therefore

$$\Delta G_{298}° = 174.47 \text{ kJ/mol} - 298 \text{ K} * .11206 \text{ kJ/mol K} = 141.09 \text{ kJ / mol}.$$

One useful thing about our equation for $\Delta G°$ is that we can use it to estimate $\Delta G°$ at other temperatures, by using

$$\Delta G_T° = \Delta H_T° - T\Delta S_T°.$$

What is really useful is that even though $\Delta H°$ and $\Delta S°$ depend on temperature, if we don't change our temperatures too much, they don't change very much, i.e., over a small enough temperature range they are essentially constant. Therefore we can write **$\Delta G_T° \cong \Delta H_{298}° - T\Delta S_{298}°$.** This is convenient because we can calculate $\Delta G°$ at different temperatures without having to calculate a new ΔH° and a new ΔS°. Again, as long as the temperature difference is not too large this is a pretty good approximation.

Let's do an example of this by calculating ΔG_{1600}° for our ethylene reaction. We already calculated that $\Delta H_{298}^\circ = 174$ kJ/mol, and $\Delta S_{298}^\circ = 112$ J/mol K. Now the standard free energy at our new temperature is simply $\Delta G_{1600}^\circ \approx \Delta H_{298}^\circ - 1600 * \Delta S_{298}^\circ = 174 \text{ kJ} - 1600 * .112 \text{ kJ / mol K} = -4.73$ kJ/mol. Since $\Delta G_{298}^\circ = +141$ kJ/mol, this is a rather dramatic change.

It is important to realize that **ΔG° does not have the same meaning as ΔG**. One difference is that ΔG depends on concentration or pressure while ΔG°, which is defined at only one pressure, does not. It is also of interest to learn exactly how ΔG depends on pressure or concentration. We learn this from the second of three tremendously important equations involving ΔG. This equation is

$$\Delta G = \Delta G^\circ + RT \ln Q_{act}.$$

In this equation ΔG° is the standard free energy of reaction, R is the gas constant, T is the temperature in K, ln stands for the natural log function, and Q is the reaction quotient calculated with activities. It is important to reiterate that in this equation we must use Q_{act}, and not for example Q_p. Another thing we need to note about this equation is the units of the gas constant. Notice that since our ΔG's are in units of kJ/mol, it is inconvenient to use the usual gas constant units of L atm/mol K. Fortunately, L-atm, which is a unit of energy, can be expressed in J. If we do this the gas constant becomes 8.314 J/mol K.

Let’s use this equation to calculate ΔG for a reaction where we start with two different sets of concentrations of our reactants and products, and see how these different concentrations affect ΔG and therefore the spontaneity of the reaction. For the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

at 298K, p_{H2} = .2 atm, p_{I2} = .2 atm and p_{HI} = .5 atm. Remember that

$$\Delta G = \Delta G° + RT \ln Q,$$

so in order to calculate ΔG we need to know ΔG° and Q.

$$\Delta G° = 2\Delta G_f°(HI) - \Delta G_f°(H_2(g)) - \Delta G_f°(I_2(g)).$$

If we look these up we find that $\Delta G_f°(HI)$ = 1.3 kJ/mol, and $\Delta G_f°(I_2(g))$ = 19.3 kJ/mol, and since $H_2(g)$ is an element in its stablest form, $\Delta G_f°(H_2(g)) = 0$. Combining these yields

$$\Delta G°_{rxn} = 2*1.3 - 19.3 = -16.7 \text{ kJ/mol.}$$

$$Q = \frac{a_{HI}{}^2}{a_{H_2}a_{I_2}} = \frac{\left(p_{HI}/1atm\right)^2}{\left(p_{H_2}/1atm\right)\left(p_{I_2}/1atm\right)} = \frac{.5^2}{.2\times.2} = 6.25$$

Combining these yields

$$\Delta G = -16.7 \text{ kJ/mol} + 8.314 \text{ J/K mol} * 298\text{K} * \ln 6.25 * 1 \text{ kJ/1000J} = -12.16 \text{ kJ/mol.}$$

Since ΔG < 0, the forward reaction, formation of HI, will be spontaneous.

What if our initial partial pressures were p_{H2} = .05 atm, p_{I2} = .025 atm and p_{HI} = 2.0 atm? Now $Q = \frac{2^2}{0.5\times 0.25} = 3200$, and ΔG = -16.7 kJ + 8.314 J/K mol * 298K * ln 3200 * 1 kJ/1000J = 3.2 kJ/mol. SINCE ΔG > 0, WHICH WILL SPONTANEOUSLY OCCUR, FORMATION OF HI, THE FORWARD REACTION, OR DECOMPOSITION OF HI, THE BACKWARD REACTION? So we see that **by using standard free energies and the reaction quotient, we can predict which direction of a reaction will be spontaneous, the forward reaction or the reverse reaction.**

Lecture 35

Let's continue looking at the equation $\Delta G = \Delta G^\circ + RT \ln Q_{act}$, and see what else we can learn from it. Let's consider a special case that is of tremendous importance in chemistry. Remember that **when $\Delta G = 0$, our system is in equilibrium**. If we plug a value of 0 for ΔG into our equation we get the equation

$$0 = \Delta G^\circ + RT \ln K_{act},$$

where K_{act}, the equilibrium constant, is the value of Q_{act} at equilibrium, i.e., $K_{act} = (Q_{act})_{eq}$. We can rewrite this as

$$\Delta G^\circ = -RT \ln K_{act},$$

which tells us that if we know K_{act}, we can calculate ΔG°. If we divide both sides of the equation by $-RT$ we get $-\Delta G^\circ/RT = \ln K_{act}$. If we now take the exponential of both sides we get

$$K_{act} = e^{-\frac{\Delta G^\circ}{RT}}$$

This equation tells us that if we know ΔG°, we can calculate K_{act}.

Let's do a couple of examples of these two calculations. **First let's calculate K_{act} from ΔG°.** First consider the reaction

$$H_2 + I_2 \rightleftharpoons 2\ HI$$

at 298K. Our equation is

$$K_{act} = e^{-\frac{\Delta G^\circ}{RT}}$$

In order to calculate K, we need to find ΔG_{298}° first. From our equation for the reaction we know that

$$\Delta G_{298}° = 2\Delta G_{f,298}°(HI) - \Delta G_{f,298}°(H_2(g)) - \Delta G_{f,298}°(I_2(g)).$$

Let’s fill in the numbers. Does anyone have their book? Open it up to the table of free energies of formation on page A-9. What's the free energy of formation of (HI, H_2, $I_2(g)$) [1.3, 0, 19.3] Now take out your calculators and tell me what $\Delta G_{298}°$ = ? [-16.7 kJ/mol] Now let’s plug this into our equation for K_{act}. WHAT VALUE OF R SHOULD WE USE HERE?]

$$K_{act} = \exp(16.7 \text{ kJ/mol}/(8.314 \text{ J/mol K} * 298\text{K}).$$

WILL THIS EQUATION WORK? WHY NOT? [Units] So we have to convert kJ to J. This gives us

$$K_{act} = \exp(16700 \text{ J/mol}/ (8.314 \text{ J/mol K} * 298 \text{ K})).$$

Why don't you all run this through your calculators and tell me what this comes out to? [846]. WHAT DOES THIS TELL US? [Products are favored.] In this case $\Delta G° < 0$ and products dominate our equilibrium mixture.

Now let’s just try other values of ΔG° and see what values of K we get. Why don't you suggest some values of ΔG° and we'll figure out what K is. Lets plug this into $K = \exp(-\Delta G°/RT)$. (Get 3 or 4 examples. Prompt for both positive and negative ΔG°, interpret using Q to show reactants or products favored.) Our conclusion is that a positive ΔG° yields a $K < 1$ and therefore favors reactants, while a negative ΔG° yields $K > 1$ and therefore favors products.

Now we can understand the difference between ΔG and ΔG°. ΔG depends on concentration. It changes its value as the reaction proceeds. We can tell whether a given reaction mixture will change spontaneously by calculating the value of ΔG. If ΔG is positive, the forward reaction will be spontaneous, while if ΔG is negative, the reverse reaction will be spontaneous. ΔG°, which is defined only at one pressure, 1 atm, or one concentration, 1 M, is a constant at a given temperature for each reaction. It does not depend on composition, and does not change as the reaction proceeds. Therefore it does not predict spontaneity. What $\Delta G°$ does tell us is whether the reactants or products will be favored when the reaction reaches equilibrium. The rule is if $\Delta G° > 0$, then reactants will dominate. If $\Delta G° < 0$ then products will dominate. Finally if $\Delta G° = 0$ neither reactants nor products will be favored.

We've just shown how to calculate K_{act} from ΔG by using $K_{act} = e^{-\Delta G°/RT}$. Let's see how to calculate $\Delta G°$ from K. Let's use the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

as an example. Suppose we begin with a mixture at 699K in which p_{H2} = .640 atm, p_{I2} = .571 atm, and P_{HI} = 0. When the reaction reaches equilibrium, the pressures are p_{H2} = .167 atm, p_{I2} = .0980 atm and p_{HI} = .946 atm. The activities will be .167, .0980 and .946 respectively, and $K_{act} = .946^2/.167 * .0980 = 54.7$. Now that we know K_{act}, we use $\Delta G° = -RT \ln K = -8.314$ J/K mol * 298 K * ln 54.7 = -9,910 J/mol = -9.9 kJ/mol. Lets try the same game we did for $\Delta G°$, and suggest values of K_{act}, and figure out what $\Delta G°$ is. [Prompt for values of K_{act} greater than and less than 1].

There are two ways that temperature effects the equilibrium constant. The first way in which **temperature affects the equilibrium constant is shown by the equation, $K = \exp(-\Delta G°/RT)$. If $\Delta G° > 0$, K will increase when the temperature increases**. For example consider a reaction with $\Delta G_{298}° = 15$ kJ/mol. At 298 K the equilibrium constant is given by

$$K_{act} = \exp(-\Delta G°/RT) = \exp(-15000\text{J/mol}/(8.314\text{ J/K mol})* (298\text{K}) = 2.35 \times 10^{-3}.$$

Now consider the same reaction at 398 K. At this temperature

$$K_{act} = \exp(-15000 J/mol)/(8.314 J/K\ mol)(398K) = 1.07 \times 10^{-2}.$$

Even though the reaction still favors reactants, shifting the temperature has moved the equilibrium more toward the product side. So we see that temperature effects equilibria. What happens when ΔG° is negative? Suppose ΔG° is -12 kJ/mol at both 298K and 398K. HOW DO WE CALCULATE K_{ACT} AT 298? WHAT IS K_{ACT}? (126.9) WHAT IS K_{ACT} AT 398K? (37.6) Notice that **when ΔG° is negative and we increase the temperature, that the equilibrium shifts toward the reactant side**.

The other reason that the equilibrium constant changes with temperature is that the standard free energy ΔG° changes when we change the temperature. The temperature dependence of ΔG° is given by the equation

$$\Delta G° = \Delta H° - T\Delta S°.$$

Let's first consider the most dramatic case, where ΔH° and ΔS° are both positive. Consider a reaction for which $\Delta H_{298}°$ = 25 kJ/mol and $\Delta S_{298}°$ = 98 J/K mol. Then $\Delta G_{298}°$ = 35 kJ/mol - 298K*.098 kJ/K mol = 5.79 kJ/mol. From our previous discussion we know that this means that reactants will be favored over products at equilibrium. Now consider the same reaction at 398K. At this temperature, $\Delta G° \approx \Delta H_{298}° - T\ \Delta S_{298}°$ = 35 kJ - 398K * .098 kJ/mol K = -4.00 kJ/mol. Since ΔG° is negative, products will be favored at this temperature. We can draw a general conclusion: **if ΔH° > 0 and ΔS° > 0, reactants will be favored at low temperatures while products will be favored at high temperatures**.

Now suppose we have a reaction where ΔH° = 75 kJ/mol, and ΔS° is negative, -25J/k mol. At 298K, ΔG° = 75 - 298 * - .025 = 82.5 kJ/mol. At 400K, ΔG° = 75 -400 * -.025 = 85 kJ/mol which is even more positive. **So we see that if ΔH° is positive and ΔS°**

is negative, ΔG° will be positive at all temperatures, and reactants will always be favored. If we do a similar analysis we find for the remaining two cases that **if ΔH° is negative and ΔS° is positive, ΔG° is negative for all temperatures and products will always be favored**. Finally, **if ΔH° is negative and ΔS° is negative, ΔG° will be negative at low temperatures and positive at high temperatures, and products will be favored at low temperatures**. To reiterate, if ΔH° is positive and ΔS° is positive, then reactants will be favored at low temperatures and products at high temperatures. If ΔH° is negative and ΔS° is negative, products will be favored at low temperatures and reactants will be favored at high temperatures. Finally, if ΔH° is positive and ΔS° is negative, reactants will always be favored, while if ΔH° is negative and ΔS° is positive, products will always be favored. So we see that we can use thermodynamics not only to predict whether reactants or products will be favored in a chemical reaction, but in addition and powerfully, whether we can use temperature to change that.

Notice that we have two distinct sources for the way temperature affects equilibrium, the change in ΔG° given by $\Delta G° \approx \Delta H_{298}° - T\Delta S_{298}°$, and the change due to the equation $K = \exp(-\Delta G°/RT)$. It would be useful if we could develop one equation that combines both of these effects. We can do this by first taking the ln of both sides of our second equation to give,

$$\ln K = -\Delta G°/RT.$$

Now we substitute ΔH° - TΔS° for ΔG° to give

$$\ln K = -\frac{(\Delta H° - T\Delta S°)}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}.$$

This is an equation for a straight line, y = mx + b, with y = ln K, m = ΔH°/R, x = 1/T, and b = ΔS°/R. If we plot ln K vs. 1/T we get a straight line. The slope of a straight line is the change in y over the change in x so we can write,

$$\frac{\ln K_2 - \ln K_1}{\frac{1}{T_2} - \frac{1}{T_1}} = -\frac{\Delta H^\circ}{R}$$

We can rewrite this as

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

We can get the other useful form of this equation by taking the exponential of both sides and multiplying it out to get

$$K_2 = K_1 e^{-\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

This gives us **the temperature dependence of the equilibrium constant.** We only need to know the original equilibrium constant and ΔH°. This equation is particularly useful, because ΔH° changes very slowly with temperature, so as long as the temperature change isn't too large, we can assume that ΔH° doesn't change when the temperature changes. Let's try using this a couple of times. [Someone give me K_1, ΔH° > 0, T_1 and T_2] Let's plug these into our equation. [What is the new K?] Let's try this for another K_1, T_1, and T_2, but this time with ΔH° < 0.

So we see that for ΔH° > 0, as T increases the equilibrium constant increases, i.e., favors products more. In contrast, if ΔH° < 0, as T increases the equilibrium constant decreases.