

Lecture 13B • 10/27/11

Thermodynamics

First, we defined what a system was – an arbitrary frame of reference. We talked about internal energy – which is a measure of the energy content within that system; it's the sum of all of motion of the different molecules in that system. We talked about how that quantity is similar to but distinct from something called enthalpy. Enthalpy is the quantity that we'll normally use when talking about thermodynamics. Enthalpy is a composite function of [raw energy] adjusted for pressure-volume work; we're trying to avoid dealing with that pressure volume work, and that's what the enthalpy function is designed for. Whenever we talk about heat of reaction, we're going to be talking about it in terms of enthalpy. There are two other terms: entropy, which is related to the homogenization of matter and energy; and free energy, which is where you take enthalpy which is the raw energy difference between reactants and products and adjust it for the effects of entropy. {kinetics}

Let's start with entropy, which is, in the simplest way to express it, disorder. A better way to say it is that is the tendency of both matter and energy to become homogenized, to become spread out through a system. ΔS is usually used to represent entropy. A good example of entropy would be in a set of chalk erasers. Imagine that you had two chalk erasers that you clapped together, generates a puff of chalk. Is it possible that that chalk is going to reorganize itself and come and it back down on the erasers. Yes it is, but it's never going to happen, because it's a statistical improbability. You'd have to get all of the molecules exactly the right way for them to be able to come back to the erasers. But, it's not technically impossible. If you think of all of the different ways those molecules could move, all the different energy states that those would result in, there are many more energy states that would cause that energy and matter to be spread out than there would for it to become concentrated. That's the idea behind what entropy is – that if you have to organize a system, that there's effective an energy penalty for that organization, because you're selecting just one of just the few energy states out of the many possibilities there might be. Another way of putting it: if whatever process you have generates disorder, allows this energy to be spread out, causes matter to be spread out, that has an energetic benefit to it, because that's what energy wants to do, anyways. So entropy, yes, is disorder, but it has an energetic consequence.

To order a system – which in terms of the sign convention, if we're talking about a system itself, if we're removing entropy, that's going to be a negative value. To order a system effectively costs energy. In a system that creates disordered or becomes disordered, from the sign convention would mean a positive value, the system itself is getting more entropy. That kind of system experiences a release in energy. This has consequences for chemical reactions. You might have a set of products that are lower in energy than reactants. Normally, you'd think that reaction should go forwards because that's downhill in energy; things roll downhill. If that process causes molecules to be heavily organized, there's an energetic penalty that might be greater than the energy benefit that you get from going from reactants to products. In other words, if we're talking about ΔH , heat of reaction, we're looking really at just a set of molecules in some sense. Entropy tells you what's really going on in solution. We combine the two, and that's a quantity called free energy (ΔG). It's the energy difference between reactants and products, adjusted for the effects of entropy. There an equation for ΔG , which is the following: it's enthalpy, ΔH , minus $T \Delta S$. Why minus? To make the effect of entropy match the sign convention for energy. Making order is a negative entropy, but that therefore costs energy, we throw a negative sign in front of that to make it a positive energy value, which means that the system is effectively having to absorb the energy. Temperature gets thrown into this equation as well because the higher the temperature that you have, the more possible energy states that you have, and, therefore, the more possibility of disorder. Free energy is really a measure of potential energy – it's really the amount of energy actually available for a chemical reaction. Potential energy, ΔG , can be related to a potential, a voltage, so there's a direct connection between the two.

We have these two different forms of energy – enthalpy and free energy. Texts often go back and forth between using both of those in certain situations. Generally, if we're focusing just on the structure of the reactants and products and how structure affects energy, we're going to normally be doing it in terms of enthalpy. Any time we use the expression heat of reaction, that's something expressed in terms of enthalpy.

Let's revisit Hess's Law. Hess's Law is the fact that an energy change in a chemical reaction is only due to what the reactants are that you start with and what the products are that you end up with, and not at all how the chemical reaction occurs. The change in energy (in terms of enthalpy) for a chemical reaction depends only on the reactants and products, and not at all on how the reaction occurs. Enthalpy is a state function. State functions are those where you look at where a system starts, where a system ends, and that's what determines what the value of the function's going to be. Displacement was our example of a state function, because only if you move the points did that distance change. Depending on how you go between those two points, that distance is entirely related to the path that is taken. The important point here is: no matter how a chemical reaction occurs, no matter how we get from those reactants to products, whether it's just a one step reaction, or whether we can assemble a sequence of reactions that end up having the same overall transformation. That energy change is going to be the same, no matter how we do it.

Another way that Hess's law is sometimes expressed is that if you do have an overall reaction that's made up of several individual reactions, the energy change of the overall reaction is equal to the sum of all those individual energy changes. So, if some larger reaction can be expressed as a sequence of smaller reactions, the energy change for the overall reaction is the sum of all of the individual reactions.

{caution about the use of the word "stable"}

Reaction coordinate diagram (RCD) – it shows the energy change of one set of reactants as they are completely converted into products. That's key: it's not necessarily a solution, it's just one molecule of the reactant and see what happens to it as it becomes a product. That's what a reaction coordinate diagram is. A reaction coordinate diagram shows the energy of one instance of a reaction, as reactants are fully converted into products.

Why is it called a reaction coordinate diagram? This diagram is an energy diagram where you're trying to figure out, how do things change as you're going from reactants to products? If we wanted to do that really systematically, we could look at the position of each atom, and allow each atom to move in whatever way it wants to, and as the coordinates of those atoms change, what's the resulting change in energy that occurs. Let's say we had two different molecules, each with five atoms, and we wanted to make a proper graph. They're very small molecules. Each of those atoms has three coordinates: x, y, and z. Three coordinates times ten atoms, that's 30 different coordinates that you could individually adjust, plus energy itself is a result of this function, so it's another coordinate on that graph. So, for two molecules with just ten atoms between them, this diagram would be 31-dimensional – and most of us are not able to think rapidly in 31 dimensions. So, what we do is say, what is the most likely pathway of a reaction. Which way would the reactants most likely react? Then, we just follow that energy change along that most likely pathway. We call that most likely pathway the reaction coordinate; that's why we call it a reaction coordinate diagram. That's why it's only a two-dimensional diagram, because we don't worry about variations; we look at the most likely pathway the reaction's going to take. Reaction coordinate is the most likely – which means the most energetically-favorable – pathway for a reaction.

Let me write up a reaction coordinate diagram. It doesn't necessarily correspond to any particular reaction; I'm just trying to show some of the features of a reaction coordinate diagram. Energy's going to be the y-axis, and, until and unless we are talking about equilibrium, I'm going to do everything in enthalpy. The diagram might look like this: traditionally, reactants are written on the left; products are written on the right. There's this hump in between, which is higher in energy than either the reactants or the products; it's the most difficult point in a reaction. That is often notated using a symbol called a double dagger; that corresponds to the transition state, which is the highest-energy point in a single elementary step. What do I mean by elementary step? One step in a chemical reaction. For example, in the S_N2 reaction, we saw a mechanism where two molecules were interacting at once, so there was a bond forming and bond breaking that were both happening as one step. In the S_N1 reaction, we had three different steps (at least in our particular example): first, an atom comes off to form a carbocation; something attacks that carbocation; and since we've so far been showing alcohols or water attacking, there's a third deprotonation step. Each of those three steps would be called an elementary step. So, the highest-energy point in one of those steps is the transition state.

There's an important quantity, which is the energy it takes to get up to that transition state, and that is activation energy – the energy needed to reach a transition state so that a reaction can occur. Think of a match – a match, we know, is flammable, but until you put friction on it by striking it against something, it doesn't burn. That energy you provide goes into the activation energy, to put the energy in necessary to get these things to react. Once you get there, this might be a somewhat appropriate diagram for that kind of case, because the products end up being lower energy than the reactants, indicated that once you get the reaction going, it's going to want to keep on going. That's the last quantity that I need to show on this diagram – the change in energy from the reactants and products, that is the heat of reaction. It's the energy of the products minus the energy of reactants.

At this point we're set up to be able to talk about kinetics.

Unless you have enough energy, maybe they start to react, bonds might be vibrating, but until you give them that energy for it to occur, it won't occur. We'll talk about an intermediate, something that can form temporarily during the progress of a reaction.

Let's switch into kinetics. To show you a slightly more complicated diagram, let me write down this: a chemical reaction may be composed of one or more elementary steps, each of which has its own transition state. I'm going to write up, not for any particular reaction, a two-step reaction coordinate diagram. I'm going to do this in terms of enthalpy; I'll show reaction coordinate as my x axis. I have the reactants and products, but now I have one other thing as well, an intermediate. As you're going along the diagram at first, a bond might be starting to break, so as you stretch that bond, you're having to add energy in. You get to that transition state, that's the high-energy point. Maybe the bond finishes breaking, then you end up with this molecule that has a definite structure, but you might not be able to isolate it from solution. A good example might be the formation of a carbocation.

You might for that positive charge, but normally we can't take just a positive charge and pull it out of solution and isolate it in a bottle. It might be something we can detect, something we might trap, and therefore show some evidence that it's forming, but you can't isolate it. That's what an intermediate would be. Some reactions, intermediates might be isolatable, most of the time, it's going to be a situation where it's not. An intermediate is a chemical species that forms during reaction, but might not be isolatable.

We still have the heat of reaction, which is the overall difference between the energy of the reactants and products. We could add up the individual steps, their energies, but the point of Hess's law is that you don't even have to look at that; just look at the start and end points, and that's the heat of reaction. We have two transition states. For each individual step, you're going to have a transition state, so number of steps, number of transition states – also, therefore, the number of different activation energies. How do we properly write activation energy when we have multiple steps? Whether it's an intermediate that you're forming or a product that you're forming, the activation energy is always measured just to the left of that transition state up to the transition state. For the first transition state, I'd go from the reactant all the way up. For the second transition state, I only go from the level of the intermediate's energy level, because if you've already made it through the first step of the reaction, you've already got that much energy, so the activation energy for that second step is not measured from the reactant – this is a key point, an often missed thing. It comes from what is just immediately before it, which in this case is that intermediate.

The fact that we do have these multiple steps with these activation energies is what can lead us into a discussion of a rate-limiting step (RLS), which is the idea that in a multistep chemical reaction, the rate of the reaction is usually controlled by one particular step. Generally, it is the step with the highest activation energy. To talk a little bit more about this, we should again refer back to what a rate law looks like. Rate in chemical reactions can be expressed as the change in concentration of some particular reactant or product over time. Technically, what I've shown you here is average rate, because you're talking about delta, you're talking about a range of time, but maybe the rate of reaction is changing at each moment. More appropriately, we really should approach this from a calculus perspective. More importantly, this rate is given by a rate law that has at least one thing in it: k , which is the rate constant; and then, one or more, or sometimes zero, concentrations of reagents. What determines what goes in this rate law? This would only be those reagents that are in that rate-limiting step. For the rest of today, what we're going to discuss is why would that rate-limiting step have an effect? What are some of the components in this rate constant? Only the reactants in the RLS are included in the rate law. If we take a simplified approach to kinetics, in all the cases we'll encounter, there's just one rate-limiting step. But, there can be cases where that approach isn't quite the right way. In most cases, if you have some notably difficult step, you can think of it this way: that all the reaction steps that happen before it, they're fast in comparison, so it's like they build up a certain amount of reactants that are just waiting to get over that most difficult step. Or, think of it the other way: after that most-difficult step, everything else is easier in comparison, so as soon as it gets made, it does its next thing. That's why, in general, it's that one step that controls rate. But if you have multiple reactions that may be happening in solution, and if there's any equilibrium that's occurring, then the situation might end up being more complicated.

Let's look at this Arrhenius expression. $k = A * e^{(-E_a / RT)}$. R is just a constant, the thermodynamic constant. A is something that we won't talk about terribly much, but it is something known as the steric factor, same type of steric that we're talking about with steric hinderance, the idea that the more difficult it is for the molecules to orient physically to react, the slower the reaction therefore will be. If it's really easy for the molecules to line up, really easy for the reaction to occur. That's effectively what's bundled up in that constant A . It's indirectly a measure of how difficult it is for molecules in a reaction to orient themselves properly.

What I want to focus on instead are the two other factors in this expression for the rate constant. Before we can do that, though, we need to talk about something known as molecular energy distribution. An example I always give for this phenomenon is vapor pressure. Think of this situation: if I were have to spilled just a few drops of water on the bench top here and nobody cleaned it up, and that room might be used as it normally is, so sometimes the air system's on, sometimes it might be off, the room might be open, the room might be closed, but if it's just a few drops of water, and we came back tomorrow, would you expect that it would be sitting around? No, but what's the boiling point of water? If you answered 100 °C, then you really you should have been answering: what pressure, because remember that boiling point depends on the surrounding pressure. So if I say what is the boiling point at atmospheric pressure, 100 °C. But is it ever going to get 100 °C in this room, short of a fire occurring? No. So how is it that water can evaporate if it's nowhere near its boiling point? Some of the molecules are moving at different energies than others. In any system of molecules, you'll have a range of speeds, a range of energies. A way to imagine that is – and this is a kinda silly example – imagine a room where you have the entire surface of the ceiling of that room covered in raquetballs or something bouncy. Now imagine that, while we're standing out of the way of all of this, I hit a button and all of those balls drop at exactly the same time. At that moment where they drop, they're all going to be travelling speed, but soon as they hit the floor or hit whatever else is in the room, they're all going to start bouncing into each other. Kinda like on a pool table, some of those ball might travel more quickly, some will travel more slowly. Same thing happens with molecules; if you had some assembly of molecules that were all moving with exactly the same speed, there is, in a technical way, no calculable temperature, because the idea of temperature is directly connected with the idea that there's a distribution of molecular energies.

This kind of graph has the following form: x-axis is energy per molecule, so looking at all of the different cases of speeds the molecule might have; y-axis is the number of molecules that have those different energies. At low temperature, the distribution tends to be narrower, and, since it's lower temperature, it's going to be lower energy per molecule. Higher temperature, higher average energy, but also a broader distribution of those energy states. Now let's say that we have some energy barrier. In the example I gave of water evaporating, we could say heat of vaporization. If we're talking about a chemical reaction, we could talk about activation energy. Let's say that I put some activation energy on this graph. Well, if the molecules have more than that activation energy, the reaction's going to occur. At low temperatures, there's only a small fraction of those molecules that have the energy to react, but at high temperatures, there's many more molecules that have that energy, so that would automatically lead to a faster rate of reaction, more molecules having enough energy to react. First, this idea of molecular energy distribution: at any temperature, there is a distribution of molecular energies caused by the constant collision of molecules with each other. As this graph shows, at higher temperature, a larger fraction of molecules would have the energy to pass over a transition state.

Temperature has an effect on the rate of reaction. But, activation energy itself has an effect. We could use a very similar diagram to demonstrate that. Let's say we had just one temperature that we were worrying about. Again, number of molecules my y-axis, energy per molecule my x-axis. Let's say here are two different activation barriers, one lower energy, one higher energy. We can see that if we move the energy barrier up that, no matter what temperature we're at, that's going to reduce the fraction of molecules that have that minimum energy. Low threshold, lots more molecules with enough energy. At the same temperature, a higher activation energy will result in fewer molecules being able to reach the transition state. This the reason why we say it's the reaction step with the highest activation barrier that's going to be that rate-limiting step, because if you have a multistep chemical reaction that's all happening at the same temperature, well then we're not worried about temperature effects. And let's say, just for the sake of argument, that there's not a huge steric difference between different steps of a reaction. Then it's going to be activation energy that determines how many molecules can successfully react. Those are the ones that end up in the rate law. Why would any concentration at all show up in a rate law? Well, more concentration, more chances that productive collisions are going to occur, which, again, mean faster rate of reaction. So the concentration of the reactants in the rate-limiting step affects the rate of reaction, because the greater the concentration, the greater change for successful molecular collisions.

Let me make a very brief summary of terminology. All of this discussion is to focus on how many reagents are in that rate-limiting step, which is how we decided to call one of those substitution mechanisms Sn2 and one of the other ones Sn1. There is this idea of reaction order, which is the number of molecules participating in an individual step. Most commonly, we're going to see first-order, which is also known as a unimolecular step, because it only involves one molecule. For example, the first step in an Sn1 reaction, that's what makes an Sn1 reaction, because that step – the one that happens to be the rate-limiting step – only has one molecule in it, so it's first-order, which we also call unimolecular. Second order, which is called bimolecular, which is why we called the Sn2 reaction Sn2; that's because we have two molecules. Somewhat rarer is a termolecular reaction, where you have third-order, where there's three molecules involved. Generally, you don't have above that, because then it becomes very difficult for that many molecules to coordinate at the same time and have some reaction step occur.

Thermodynamics (con't), kinetics

Entropy (ΔS) – disorder – tendency for both matter and energy to become homogenized.

– to order a system ($\Delta S < 0$) effectively costs energy, and a system that becomes disordered ($\Delta S > 0$) experiences an effective release in energy

Free energy (ΔG) – the energy difference between a set of reactants and products, adjusted for the effects of entropy. $\Delta G = \Delta H - T \Delta S$

potential energy – the amount of energy actually available to/from a chemical reaction

heat of rxn – enthalpy

equilibrium – free energy

Hess's Law – the change in energy (ΔH) for a chemical reaction depends only on the identity of the reactants and products, and not at all on how the reaction occurs.

enthalpy is a state function.

– If a larger rxn can be expressed as a sequence of smaller reactions, the energy change for the overall reaction is the sum of all of the individual reactions.

Reaction coordinate diagram (RCD)

– Shows the energy of one instance of a chemical rxn as reactants are fully converted into products

reaction coordinate – the most likely (most energetically-favorable) pathway for a reaction

transition state – highest energy point in a single elementary step

Activation energy (E_a) – the energy needed to reach the transition state so that a rxn can occur.

$\Delta H_{rxn} = E_{products} - E_{reactants}$

Kinetics

– A chemical reaction may be composed of one or more elementary steps, each of which will have its own transition state intermediate – a chemical species that forms during a reaction but might not be isolatable.

Rate-limiting Step (RLS) – In a multistep chemical reaction, the rate of reaction is normally controlled by one particular step – generally, it is the step with highest activation energy.

Rate: $R = \frac{\Delta \text{reactant}}{\Delta T} = k[A]^a[B]^b \dots$

k – rate constant

*Only the reactants in the RLS are included in the rate law

$k = Ae^{(-E_a/RT)}$: Arrhenius expression

A: steric factor – how difficult is it for the molecules to orient themselves properly in order to react

Molecular energy distribution – At any temperature, there is a distribution of different molecular energies caused by the constant collision of molecules with each other.

At higher T, a larger fraction of molecules would have the energy to pass over a transition state.

– At the same T, a higher E_a will result in fewer molecules able to reach the transition state.

[] of the reactants in the RLS affects rate because the greater the concentration, the greater the chance for successful molecular collisions.

Reaction order - # of molecules participating in an individual step.

1st order – unimolecular – only one molecule

2nd order – bimolecular – 2 molecules

3rd order – termolecular – 3 molecules