Lecture 13A • 10/26/11

We talked about a system, a frame of reference; internal energy, which is the energy content inside that system; how it[internal energy]'s distinct from this thing called enthalpy, which is a function that lets us not worry about work, so we can only focus on the raw energy difference in reactants and products as we're trying to conduct a chemical reaction; state function, contrasted with a path function, Hess's law.

Entropy and free energy.

Let me tackle entropy first. Entropy is usually thought of as disorder, which it is, but in a more sophisticated way, it is the tendency for both matter and energy to become homogenized, spread out. One example: if you have two chalk erasers, you clap the two erasers together, and the chalk is going to spread out, that's what we're used to. Is it possible that all of that chalk is going to come back and rearrange itself on the eraser afterwards? Yes, it is possible, but it will never happen in our lifetime. For all of those molecules to coordinate themselves suddenly to be able to come back to that initial starting place, just not likely. The same thing is effectively true of energy. If somehow you have energy concentrated at one part of your solution, that energy's going to end up spreading out. That's what really entropy represents: that, if you try to order a system – this is not talking about individual chemical reactions, this is something that applies to entire solutions – if you have an entire solution, then if you're trying to order it, it's going to effectively cost energy to cause that ordering. Other way around, if the process causes energy and matter to be spread out, that's what it wants to do anyways, so it actually costs less than you think it would for that process to occur. Ordering a system or disordering a system has an energy content that is effectively associated with it; that's what entropy represents. To order a system, to bring order to a system, effectively costs energy; a system that creates disorder effectively experiences a release in energy. Entropy is more a phenomenon of reactions in solution, and it's not so much applicable to individual chemical reactions.

Because there is this cost that's effectively associated – or benefit that might be associated – with things becoming either ordered or disordered, we have yet one more combination function which is called free energy. Free energy is the raw difference – if we're talking about chemical reactions – the raw difference in energy of a set of reactants and products, adjusted for the effects of entropy. Entropy is usually expressed as S, and free energy is usually expressed as G. So delta G is enthalpy – which we are going to treat as the raw energy content of a reaction – adjusted for these either detrimental or beneficial effects of entropy. If making a mess is effectively a release of energy, then entropy – that positive increase in disorder – we need to throw a negative sign in front of it in order to match our sign convention. A system that is getting disordered, that is positive enropy, so delta S > 0 means increasing entropy. delta S < 0 means decreasing entropy. Common example, non-chemical reaction example: you go from a liquid to a gas, the molecules become much more disperse; that's positive entropy. If you freeze something, you're coordinating the molecules together, that's a decrease in entropy. To match the sign convention of energy, through, we throw this negative sign in front of it. There is also an effect related to temperature: the hotter a system is, the more possible energy states there are, the more possible ways there are for energy to be distributed, so the effect of entropy increases – whether favorably or unfavorably – as temperature goes up.

What is really the difference between enthalpy and free energy? Enthalpy, you look at a set of reactants, you look at a set of products, kinda ignore what physically may be going on as those molecules react, you just look at the raw energy content of the reactants and products – raw energy difference. In real reaction, there is this entropy effect that you do have to worry about. Once you've adjusted for it, the delta G, that really is equivalent to potential energy [of the system], the amount of energy actually available for a chemical reaction. There is a relationship between this [free energy] and potential, in terms of an electrochemical reaction – in other words, voltage.

We often will only be worried about a compound's energy; if we're talking about individual compounds that are not even reacting, we don't necessarily worry about entropy. Or, even if entropy is in effect, we can choose whether we're going to just focus on this energy difference, or whether we're going to worry about how energy is spread around in a chemical reaction. Equilibrium is related to potential energy, so there we must use delta G. Any time we just say heat of reaction, that means the energy difference, which means we'll be dealing with enthalpy. Heat of reaction – enthalpy. Equilibrium, which is indirectly related to potential energy – free energy.

Hess's Law – the fact that the change in energy, delta H, for a chemical reaction depends only on the identity of the reactants and products, not at all on how the reaction occurs. Enthalpy is a state function – that's exactly what a state function is. It doesn't matter how you get from point A to point B, it matters where is point A, where is point B. What kind of reactants do you have? What kind of products do you have? Another way this is sometimes expressed: if multiple individual reactions add up to some greater overall reaction, the energy change in that overall reaction can be determined just by adding up all the individual reactions.

Reaction coordinate diagram (RCD)

A reaction coordinate diagram shows the energy of one instance of a chemical reaction as the reactants are fully converted to products. What do I mean by that? It means you don't have a mole of something reacting with a mole of something. This is treating it as a molecule-by-molecule basis. If I had t-pentyl alcohol reacting with hydrochloric acid to make the t-pentyl chloride, the reaction coordinate diagram would map that energy change. What is this reaction coordinate? It ends up being the x-axis of our diagram. Imagine that we had two molecules that were reacting. We could try to figure out the positions of each of the atoms in those molecules, and we could calculate by a computer model what the energy change would be if we allowed one atom to move one way and another atom to move, and another atom to move. In theory, we could come up with this graph that shows all the different positions of the atoms that are possible and shows what the energy would be as we changed each one of those coordinates. But for each atom, there is an x, y, and z coordinate, and if you had, say, two simple molecules, maybe each one only has five atoms. That's ten times three, that's 30 different coordinates that you're chasing around, seeing how energy would change. Energy itself would be a coordinate on that graph, so for a ten-atom system, you'd have a 31-dimensional graph – and most of us can't think in 31 dimensions. So what we do instead is we simplify and say: imagine that a reaction follows the most energetically-likely, most energetically-favorable pathway of a reaction. That is the reaction coordinate. So coordinate means like position, except we're making this fake coordinate that's just following which way the reaction is most likely to occur. It's the most likely, the most energetically-favorable, pathway for a reaction.

Let me draw a simple reaction coordinate diagram. Energy is our y-axis, and it technically could be either delta H or delta G. If we're talking about heat of reaction, that means we're dealing with enthalpy. Most of the time, therefore, we'll be using delta H as our energy scale. On the left, it's traditional that we put reactants, and on the right, we have products. At any point in a simple chemical reaction, even a one-step reaction, as you start to break bonds or form bonds there's going to be some intermediate point where you haven't quite done either yet. If you're starting to break bonds, that means that the system is becoming higher energy because you have to add energy in to break that bond. Maybe a bond is forming, but it hasn't really done so yet, so you haven't really gotten whatever stabilization you might get. That midpoint, where you reach the highest-energy point during an individual reaction step, that's what at the top of this diagram. It's often labelled with a double dagger, it's an old typographical symbol. That is the transition state.

We can label a few important quantities on this diagram. One is: how much energy does it take to get from the reactants up to that transition state. That is something called the activation energy, Ea. It is the energy needed to reach the transition state for a reaction to be possible. If you have a match, the match is not going to light all by itself at room temperature. But apply a little friction to it by striking it against a matchbox, and then the match will light up. That's because you're putting in this energy to get the chemical reaction over this transition state. Once it's past that, what happens next depends on the reactants and products. In this case, you can see that we have a decrease in energy between the reactants and products; that is delta H, the heat of reaction. Since Hess's law says that the energy change in a chemical reaction does not matter how that chemical reaction occurs, we can say, conceptually, that the heat of reaction is the difference in energy of products and reactants. It would technically be the energy of the products minus the energy of reactants, so that if the products have less energy, we report this as a negative energy change, that energy is released during the chemical reaction.

Now that we have this graph, let's talk a little bit about kinetics. A chemical reaction may be composed of one or more elementary steps, each of which will have its own transition state. For example, in the Sn1 reaction that we've seen, the reaction has three individual steps. A chemical reaction could have a sequence of individual steps; maybe one step's a bond forming, another step's a bond breaking. Sometimes you might have both processes occurring at the same time. Let's say I wanted to reason out and figure what might a multistep diagram look like. We still have the reaction coordinate; we're still going to be talking about energy changes, in terms of enthalpy. We still have the overall heat of reaction. It is still negative in this case. But now, instead of just a reactant and product, I also have an intermediate, which is a chemical species that forms during a reaction but might not be isolatable. For example, in the Sn1 reaction, the first step is to form a carbocation. Usually, it's not possible to bottle up a free carbocation. It is something distinct that forms while the reaction occurs, we just can't isolate it. That's what an intermediate would be – a stop-off point on the way to the final product. Since this has two transition states in it, it has two reaction steps. The number of transition states equal the number of reaction steps. How do you draw activation energy when you've got multiple activation energies? It's always from what's just to the left of the transitions state – either the reactant if you're starting at the beginning, or the intermediate if you're starting from that point – you start from that energy point and go up to the transition state. What's often [incorrectly done] is that I'll see students draw from the reactants and drawing activation energy up to the second transition state. Realize that if you're doing this chemical reaction, you're already going to be at the intermediate, so you don't have to add that full amount of energy to get to the second transition state because you've already added it in. So it's always from just left of the transition state up to the transition state itself.

Where this leads into kinetics is that we have these different steps that, you could say, have different amounts of difficulty associated with it. We, as humans, for example, why would we create things like elevators or, more particularly, remote controls, if we didn't care about expending as little energy as possible. Chemical systems, the same thing: it's how much energy that you have to put in that's going to control a chemical reaction. This is where this idea of the rate-limiting step comes from (RLS). In a multistep chemical reaction, the rate of reaction is normally controlled by one particular step, the most difficult step in the sequence. Generally, this is the step with the highest activation energy.

Rate law {method of initial rates; integrated rate laws}

Rate, in chemical terms, is generally expressed as the change in concentration of a reactant versus the change in time. This is technically the average rate. If you were doing this more properly, you would need to express this as a differential, which would give you the instantaneous rate. What I'm really just trying to show is how much concentration change within a certain amount of time; that's what rate is. What factors influence rate? There are two things, one of which is always in a rate expression, one of which depends on how a reaction occurs. You have this thing called the rate constant, and you have one or more – or occasionally, zero – reactants that end up going in this rate low. How do we know which reactants go in the rate law? Turns out to be the ones that are in that rate-limiting step. {iodine clock experiment} Only the reactants in the rate-limiting step are included in the rate law. Sometimes this is a simplification; sometimes you might have several competing steps. But, in general, for simpler chemical reactions, it's going to be that one toughest step that, if you can get past it, every other step in comparison is quick. Sometimes we will worry about steps leading up to the rate-limiting step. We'll say that those happen quickly in comparison, so you're generating all of this stuff, and once it gets through the rate-limiting step, then the reaction just progresses, so it's the rate-limiting step that's controlling the reaction rate. The other way to look at it is: whatever steps come afterwards, if they have lower activation barriers, they're going to end up being, generally, quicker reactions, so as soon as that product that results from the rate-limiting step forms, it goes off on its merry way. Again, it's generally that rate-limiting step that controls the rate of reaction.

What are the things that do go into this rate constant? There is an expression that can be used: the Arrhenius expressions. There are three factors that go into this, one of which we're hardly going to talk about. It's called the steric factor – it represents how difficult is it, physically, for the molecules to coordinate geometry-wise and react. What we're instead going to focus on are these other two factors: activation energy and temperature. In this context, I need to show you this graph, and let me present a situation I always give when describing this phenomenon.

Imagine that I spilled some water on the table here. The room, sometimes it's open, sometimes it's closed, maybe the air conditioner system's going, sometime's it's not, the temperature stays roughly constant. When I come back tomorrow, if it's just a few drops of water that I spilled out on the table, would you expect that it would still be there, assuming no one cleaned it up? What is the boiling point of water? You have to say to that, "what pressure?", because boiling point depends directly on atmospheric pressure. If I saw what is the boiling point of water at atmospheric pressure, 100° C. Does this room ever get to 100° C? Then why in the world is water able to evaporate, which means in some sense it's kinda like it's boiling, but it's nowhere its boiling point. How's that physically possible? And don't tell me it's because the wind can blow across it, because yes, that might be involved, but what's going on that those molecules are still able to escape? Vapor pressure. What is vapor pressure? That in a sample of molecules, some are going to be moving quickly, some are going to be moving slowly. If you have enough that are moving fast enough, those are the molecules that are going to be able to escape, for example, from the surface of a liquid. That's what causes vapor pressure – molecular energy distribution. Another way that I explain this: imagine you had a room and you covered the entire [ceiling] of that room with raquette balls or something else that's really bouncy, and you had a button where you could release all of those balls at one. At that one moment, all of them would be moving with roughly the same velocity, they're all going to be headed down, and if you could release them perfectly in unison, they should all drop at the same time. But as soon as they hit the floor, they're going to start bouncing around all over the place. When they do, they're going to adjust and end up with a distribution of speeds. Temperature itself depends on a set of molecules having an energy distribution. Quite technically, if you have a set of molecules all of which are moving at the same speed, there's no calculable temperature. There's a calculable energy, but temperature is based on this idea that there's always a distribution of molecular energies. That's what this diagram represents.

I've done one diagram in blue; I've now done another one in red. In this diagram, the y-axis is the number of molecules, and the x-axis would be the energy per molecule. At any temperature, there is a distribution of different molecular energies, caused by the constant collision of molecules with each other.

Temperature itself is kinetic energy. The fact that you have a molecule that has movement, that is temperature. To have temperature means you have kinetic energy. Unless you're at absolute zero, molecules can always technically wiggle and vibrate. Even in solids, if you zoom, there's molecular motion there, it's just constrained, that's why it's a solid. {glass}

Because these molecules are constantly bumping into each other, you're going to have different kinetic energies no matter what temperature that you're at. At higher temperatures, the distribution becomes broader. Let's say that we have an activation barrier, an activation energy. At low temperature, there's only going to be a small number of molecules that have the energy to be able to react. Increase the temperature, the distribution shifts higher: more energy, more temperature, the two go together. You have a much large fraction of molecules that would be able to pass over this activation barrier. That's why temperature is one of the variables that go into the Arrhenius expression. At higher temperature, a larger fraction of molecules would have the energy to pass over a transition state. If you called it heat of evaporation, you could say that molecules, if they have that much energy, they'll evaporate. At room temperature, only a small fraction of molecules can escape, which is why at room temperature, it does evaporate, but it takes forever. Higher temperature, more molecules with that energy, more evaporation.

A very similar diagram. If you were talking about being at just one temperature, but you talked about two different activation barriers, a lower barrier and a much higher one; let's say they were two different activation barriers for a particular chemical reaction. Well, the low barrier, you've going to have many more molecules that would have the energy to pass over. At higher temperature, very few molecules would have that energy. So if we're looking at number of molecules, the energy per molecule, then would could say at the same temperature, a higher activation energy will result in fewer molecules able to react the transition state. Along that same line of reasoning, if we ignore the steric factor, and if we are comparing individual reaction steps that are all happening at the same temperature, then that's why the rate-limiting step is the one with the highest activation energy.

Why is concentration in the rate laws? More molecules floating around, more collisions, more chance for a chemical reaction to occurs. The concentration of the reactants in the rate-limiting step affects rate because, the greater the concentration, the greater the chance for successful molecular collisions.

For an overall reaction, when you're writing the rate law, the activation energy would be corresponding to the one that's the rate-limting step.

Let me tie this back to that Sn1/Sn2 lecture. We have this idea of reaction order, which is really the molecules participating in an individual reaction step. If you have first-order, that's really saying the same thing as unimolecular, which means only one molecule involved. Second-order, which we call bimolecular, is for two molecules. Third order, termolecular, is when three molecules are involved. It's somewhat unusual to have more than that number of molecules, cause it would be hard for all of them to physically coordinate in space at the same time. We're generally limited to talking about first-, second-, and third-order – or sometimes, zero-order processes, although that will be rare for us in o-chem.

Since in the most difficult step for Sn2 two molecules are involved at the same time, that's why it's called Sn2, that's why it's called a bimolecular reaction. For Sn1, since it's multistep, but only one of those is the most difficult step, then that's why it's called unimolecular because in that most difficult step, only one molecule is involved.

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entropy, free energy, Hess's Law, stable, kinetics

Entropy – disorder – the tendency for both matter (delta S) and energy to become homogenized.
– to order a system effectively costs energy, and a system that creates disorder effectively experiences a release in energy
Free energy – the raw difference in energy of a set of reactants and products adjusted for the effects of entropy. delta G = delta H – T delta S
delta S>0 increasing entropy; delta S<0 decreasing entropy
potential energy – amount of energy actually available for a chemical reaction
heat of reaction – enthalpy
equilibrium – free energy

Hess's Law – the change in energy (delta H) 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 individual reactions.

Reaction coordinate diagram (RCD)
– Shows the energy of one instance of a chemical rxn as reactants are fully converted into products
reaction coorinate – the most likely (most energetically-favorable) pathway for a reaction
Activation energy (Ea) – the energy needed to reach the transition state for a rxn to be possible.
delta Hrxn = difference in energy of products and reactants = Eproducts – Ereactants

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.
# of transition states = # of reaction steps
Rate-limiting Step (RLS) – In a multistep chemical reaction, the rate of reaction is normally controlled by one particular step, the most "difficult" step in the sequence – generally, it is the step with highest activation energy.
Rate: R = delta reactant / delta T (average rate) or R = little delta reactant / little delta T (instantaneous rate)
R = k[A]^a[B]^B....
k – rate constant
*Only the reactants in the RLS are included in the rate law

k = Ae^(–Ea/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 Ea will result in fewer molecules able to reach the transition state.
– The RLS is the step with the largest Ea.
[] 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 reaction step.
1st order – unimolecular – only one molecule
2nd order – bimolecular – 2 molecules
3rd order – termolecular – 3 molecules