Lecture 12B • 10/25/11

Frameworks of reaction – thermodynamics, kinetics, and equilibrium

We need to start with what a system is. What is a system in thermodynamic terms? For chemical applications, what do you think a system is? There's this idea that there is a local environment and something else that we call the surroundings. In fact, the system is anything that you want it to be; it's just an arbitrary frame of reference. Normally for chemical reactions, it would be the chemicals involved in that reaction and maybe the solvent their dissolved in, but it would exclude the glassware and anything else; that, we would call the surroundings. So, a system is an arbitrary frame of reference; arbitrary means you define it like you want to define it. If we're talking about chemical reactions, it's usually the reaction mixture.

We have the system, and then we have the surroundings. What we're worried about in thermodynamics is keeping track of energy as it enters or leaves the system. That energy, we have the term internal energy (U). What is the form of that internal energy? If you heat something up, what's happening to it? It's kinda the same idea as thermal energy, where you've got all of these molecules that are wiggling around; it's a form of kinetic energy. It's not something you can directly measure, cause you're talking about the sum of all of the different kind of motions in all of the bonds and all of the molecules within a system. It is, in fact, the total of all vibrational, rotational, and translational motion of all matter within the system. Internal energy cannot be directly measured, but changes in internal energy can be measured. So if I had some metal block, for example, I can't put a probe in it and say here's its total internal energy, but I could measure the energy that's being put in that block to change its temperature.

If we're going to be talking about changing internal energy, we have to at least briefly reference the first law of thermodynamics: you can't create something from nothing – more technically, within a closed system, which is a system within which neither matter nor energy can cross the barrier of that system. Within a closed system, neither energy nor matter can be created or destroyed. In a more modern sense, you'd say the combination of energy and matter has to remain constant, since energy and matter are interconvertible. Within a closed system, which is a system that does not allow energy or matter across the system boundaries, change in internal energy is zero – you can't create something from nothing, can't destroy it. But, there's no restriction on what happens within that system; energy can change forms. This is the idea behind calorimetry. You had a styrofoam cup that you treated as if it was some sort of sophisticated isolated system – that whatever chemical reaction you were doing inside of that cup, that energy was absorbed just by the water. You used the first law as the foundation of that experiment. More generally, we could say that internal energy could be changed by one of two things: heat, in the form of temperature; or, work, which generally refers to pressure volume (PV) work. Change in internal energy is due to heat (q) and/or work (w).

Imagine that you have some kind of chemical reaction that produces a gas. If that gas was going to expand, then it's going to fight against whatever atmospheric pressure is around it. To push back against that surrounding atmosphere requires energy, requires work. So, expansion or contraction of gasses is what constitutes a large portion of the work in chemical systems. If we don't want to have to worry about that work, then there's a combination function that we can come up with. If we take the change in internal energy and we factor back in the work or factor back out, then this is something defined as enthalpy. Enthalpy is a measure of internal energy adjusted for pressure-volume work. In many cases, enthalpy is exactly the same thing as internal energy. If you had a chemical reaction that's done at constant pressure and all you have is liquids, and the volume of the solution doesn't change at all, then the enthalpy is internal energy. That's why, many times instead of saying the enthalpy of reaction we'll, in a lazy way, say heat of reaction, cause it's pretty much equivalent (but technically not). Because we're making this adjustment for PV work, we don't have to worry about it. We can say this is the raw energy of the reactants or products. Any time we're dealing with chemical reactions and we're talking about changes in energy, we're going to discuss it in terms of enthalpy. The main advantage is that we don't have to, on a case-by-case basis, worry about work; it's already built into that value. All of the related tables in your textbook already have that included.

To sum up, we have the idea of a system, that there's some arbitrary set of boundaries that we establish, and we worry about energy coming into or out of that system. Most of the time, it's going to be the chemicals in a chemical reaction. When we're discussing that energy change, we're usually going to do so in the terms of enthalpy, which is nearly the same thing as internal energy; it's just got this fudge factor built in so that we don't have to worry about any kind of work that might be involved.

The sign convention

Two very common things that happen with chemicals is that they're going to have bonds broken or bonds formed. From the perspective of a molecule, if you break a bond, is that going to require an input of energy, or is that going to release energy? From the perspective of a molecule, if you break a bond, it's going to absorb energy, because breaking a bond is not a favorable process. The only reason a bond forms in the first place is because it's going to release energy; so, turn that back around, if you break a bond, then you're going to have to input energy into it. The sign convention in thermodynamics is like this: in a case where energy is being absorbed by a system, we say that's a positive energy change, because energy is being put in the system.

What is the term for this kind of process, where energy is absorbed? Endothermic. That is when energy is added to the system. The opposite would be if energy is released from the system. For example, if you form a bond, when you form a bond that releases energy that has to go somewhere – it goes out side the molecule, outside of what is normally defined the system, so that would be a case of something being called exothermic, that energy is released from the system.

{entropy and free energy}

Enthalpy is a state function. Before we talk about what is a state function, let's define a state (not California). What is a state? The way in which energy is configured? More generally, it's all the physical descriptions of a system, for example, temperature, pressure, volume, location – some measurable aspect of that system, all those things put together is its state. A state is the set of all physical descriptions of a system. This is what a state is: its description. If we have a function called a state function, what does that mean about that equation? It depends only on those things, meaning: you look at where the system starts, its initial state, and you look at the end of that state, the end of that system. It doesn't matter at all what happens in between, the change is completely independent of that; we just worry where we start, and where we end up. A state function is a function the value of which only depends on the initial and final states, not at all on how the process occurs. Its opposite would be a function, which is a function the value of which entirely depends on ho a process occurs, and not necessarily on its initial and final states.

Let me give you a quick example of this. The example I always give is of displacement versus distance. Displacement is the following. Let's say that in order to be awake enough for your quiz, you needed to get some caffeine. One of the nearby places, for example, would be coffee society. I could ask you: what is the shortest distance between here and Coffee Society. The shortest distance is the proverbial straight line. That's displacement, the overall difference between two points. If I'm asking what the displacement is, if I'm asking what the shortest distance is, it doesn't mean how do you get there, what pathway can you take, it means, physically, how far apart are they from each other? What's the only way you can change the distance between here and Coffee Society? Move here or the Coffee Society. In other words, you have to move one of the points; you have to move either the initial or the final state. It doesn't matter how you get from one to the other, cause that's not what the question is asking. The opposite would be total distance travelled. You can't walk straight from here to there, there are going to be some turns in your path. Depending on your unique path that you take, the distance is going to change. That's nota state function, that's a path function, because it entirely depends on how you go. In theory, the shortest that could be is that distance between two points (if there's nothing obstructing you); otherwise, it could be infinity; you could go around around as many times as you want before you end up there.

Why does this relate back to enthalpy? What's so important about enthalpy? Enthalpy, being a state function, means it doesn't matter how you synthesize the reactants, it doesn't matter how you synthesize the products, they'll always have that same enthalpy. If you have reactants converting into products, that energy change during the reaction is independent of how the reaction occurs. That's Hess's law. Another way of saying Hess's Law is that if you have multiple reactions that add up to a bigger reaction, just add the energies. That's the same thing: the start point and the end point, if they're the same, it doesn't matter how you get between them; that energy change is the same.

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system, internal energy, enthalpy, entropy, free energy, state functions, Hess's law

system – an arbitrary frame of reference – in chemistry, it is usually the reaction mixture (excluding the glassware containing it)
internal energy (U) – the total of all the vibrational, rotational, and translational motion of all matter within the system.
– Internal energy cannot be directly measured, but changes in internal energy can be measured
1st law of thermodynamics – within a closed system (a system that does not allow energy or matter to flow across the system boundaries) delta U = 0
delta U = q + w. The change in internal energy is due to heat (q) and work (w).
delta H = delta U + pV
Enthalpy (delta H) – A measure of internal energy adjusted for any pressure-volume work – raw energy of reactants or products.

Sign convention
delta H > 0 – endothermic – energy is added to the system.
delta H < 0 – exothermic – energy is release from the system.

Enthalpy is a state function.
State – the set of all physical descriptions of a system. Ex: P, V, T, x.
state function – a function the value of which only depends on the initial and final states, not on how the process occurred.
path function – a function the value of which entire depends on how a process occurs and not necessarily on its initial or final states.