

## Lecture 12A • 10/24/11

### Thermodynamics

There's this word stable that we're going to throw around a lot: this carbocation is more stable than that one, or this alkene is more likely to form because it's more stable. There's a very rigorous time, definition for when you can use that word stable and be secure in using that term.

What is a system? When you're referring to a system in thermodynamics, what does that mean? Solution? Not the surroundings? What you're trying to observe? It is anything that you want it to be. It is a frame of reference. It does define an interior, which is the system, and everything which is not that, which we call the surroundings. The system is an arbitrary frame of reference. In chemistry, it is usually a solution, which means it excludes the glassware containing the solution. What is internal energy ( $U$ )? How is it different from kinetic energy or potential energy? Or is it different? It's sorta kinetic energy, but it's really the sum total of all of the vibrational, rotational, and translational motion of all matter within the system. It is similar to the definition of heat – this magic thing that gets transferred that really is energy in the form of molecular motion. Internal energy is not a directly measurable quantity; we can't stick a probe in and get the total internal energy content. However, we can measure changes in internal energy.

Related to this, we have the first law of thermodynamics: energy is conserved; energy and matter are conserved in a closed system. If we have a system, the boundary of which doesn't let matter get in or out, it doesn't let energy get in or out, then first law says the total energy of the system is going to remain constant, cause you're not letting anything in or out. In other words, energy doesn't get created from nothing; empty space doesn't turn into energy. Within that system, the energy can change forms, but it won't change its total, within a closed system, a system that does not allow energy or matter to flow across the system boundaries. Within a closed system, the change in internal energy is equal to zero. We use this in calorimetry when we pretend that those oh-so-scientific styrofoam cups are their own perfect little closed systems. We imagine that a chemical reaction going on is releasing energy, and the water in that system is absorbing the energy and the two balance each other out. Not really true, but the way that we teach the lab, we make that simplification.

More generally, the change in internal energy can be ascribed to two quantities: heat and work. Heat is, again, also this wiggling of molecules. If you have faster molecules that are bumping into slow ones, some of that energy is transferred and that is heat, that is what  $q$  is.  $w$  is work, which most generally refers to mechanical work. Particularly in chemical reactions, it's in the form of pressure-volume work.

Instead of internal energy ( $U$ ), we're going to talk instead about enthalpy. Enthalpy,  $\Delta H$ , is a measure of internal energy adjusted for any pressure-volume work.  $\Delta H$  is equal to  $\Delta U$  plus  $PV$ . The practical use of it is that it's the raw energy of reactants or products; that's how we're going to use it in chemical reactions. If we had bonds breaking, we're going to have to add energy in to break those bonds. If you had bonds forming, that's going to cause a release of energy. We need to worry about when you add energy in or release energy, from the system's perspective, do we call that plus values or minus values? What is the sign convention? If we have  $\Delta H$  greater than zero, what does that mean? Energy is being added into the system, which gives rise to the term endothermic. Which process would be endothermic? Bond formation, or bond breaking, from the perspective of the molecule involved? Bond-breaking would be endothermic, because you have to add energy into the system in order to break that bond. The opposite is  $\Delta H$  less than zero, negative, which means exothermic – energy is released from the system. The example would be to form a bond. If you form a bond, the molecules's going to end up in lower energy. That energy goes somewhere, outside the molecules, so from the molecule's perspective, to form a bond is an exothermic process.

How are internal energy and enthalpy two different quantities? Because if you had a gas that expanded, for example, that gas has to fight against the surrounding atmosphere, which means there's work involved with that expansion. But, so that we don't have to go around in every chemical reaction and worry about measuring expansions, the term enthalpy was created, where effectively you ignore the work that goes into it; it's already taken into account. In concept, all you have to know is internal energy and enthalpy, they're both measuring energy content, but enthalpy you kinda ignore the work part of it.

Enthalpy is a state function. What is a state function? It does not matter the path we take to determine the value of the function; all that matters is the initial and final state of the system. Before I define a state function, what is a state? California, Texas? In chemical terms, in thermodynamic terms? The set of all physical descriptions of a system. Some examples: pressure, volume, temperature. If you changed temperature, you're changing energy content, you're changing the system. Position, in some cases, could be a state. It's however you can describe that system – that is its state. A state function is a function the value of which only depends on the initial and final states, not on how the process occurred. It's contrast is a path function, which is a function the value of which entirely depends on how a process occurs, and not on its initial or final states.

Why do we care what a state function is? Why do we care about the fact that enthalpy is a state function? Why is that important? Hess's law says that the energy change in a chemical reaction depends only on its reactants and products, not how the reaction occurs. That, in itself, is a statement of a state function – that if you have a set of reactants, it doesn't matter how you made those reactants, their energy content depends on their identity and nothing else. Then you have the products, whose energy content only depends on the identity, not how were the products made. If you had this energy content that's unique to just its identity and you have this content, it doesn't matter if it takes you one reaction, twenty reactions, twenty different kinds of possibilities of reactions to get between the reactants and products, that energy value is always constant. That means we can predict energy changes in a reaction. Since it doesn't matter how the reaction occurs, all that matters is what's in the reaction, then that's the only reason we can predict energy changes. If every chemical reaction had a different energy quantity associated with it for every possible way to do a chemical reaction, you couldn't predict anything. So, fundamentally in chemistry, it's super important that enthalpy is a state function.

Let me give you an example of a state function and a path function, since enthalpy is a little bit abstract. The example I always give is one of distance versus displacement. If I say that we are here at De Anza; in order for some of you to survive the quiz, the only way you could do it is with caffeine, so let's say we have coffee society across the street there. If I ask you: what is the shortest distance, not physically how you walk it, but just geographically, what is the shortest distance between these two points, the proverbial answer is a straight line. That is displacement, which is the shortest distance. What is the only way I can change that displacement? Move the location. In other words, that displacement was determined by where do I start, what was my state, and where did I end, what was my final state? No matter how I walk it, the question is not being asked how much distance does it take to get from here to there; the question is asking what is the separation of those two points. Unless we have an earthquake that shifts the earth or something else happens, those two points don't move, so that distance doesn't change.

But now, if I ask you about your total distance – you have to walk around buildings, and maybe you take some kind of detour. That total distance, the shortest possible distance that could be is the displacement itself, but it could be anything aside from that as well, anything longer. Depending on what path you take, it exactly determines what this total distance is. Work is a path function; it matters how does the work occur to tell you the quantity of [energy] that's involved. Enthalpy, energy content, is a state function.

---

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

system – an arbitrary frame of reference – in chemistry, it is usually a solution (excluding the glassware containing the solution)  
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).

Enthalpy ( $\Delta H$ ) – A measure of internal energy adjusted for any pressure-volume work.  $\Delta H = \Delta U + pV$  – raw energy of reactants or products.

$\Delta H > 0$  – 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.

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 in its initial or final states.