Thermodynamic Laws that Explain Systems

A thermodynamic system is one that interacts and exchanges energy with the area around it. The exchange and transfer need to happen in at least two ways. At least one way must be the transfer of heat. If the thermodynamic system is "in equilibrium," it can't change its state or status without interacting with its environment. Simply put, if you're in equilibrium, you're a "happy system," just minding your own business. You can't really do anything. If you do, you have to interact with the world around you.

A Zeroth Law?

The zeroth law of thermodynamics will be our starting point. We're not really sure why this law is the zeroth. We think scientists had "first" and "second" for a long time, but this new one was so important it should come before the others. And voila! Law Number Zero! Here's what it says: When two systems are sitting in equilibrium with a third system, they are also in thermal equilibrium with each other.

In English: systems "One" and "Two" are each in equilibrium with "Three." That means they each have the same energy content as "Three". But if THAT’S true, then all the values found in "Three", match those in both "One" and "Two". It’s obvious, then, that the values of "One" and "Two" must ALSO match. This means that "One" and "Two" have to be in equilibrium with each other.

A First Law

The first law of thermodynamics is a little simpler. The first law states that when heat is added to a system, some of that energy stays in the system and some leaves the system. The energy that leaves does work on the area around it. Energy that stays in the system creates an increase in the internal energy of the system.

In English: you have a pot of water at room temperature. You add some heat to the system. First, the temperature and energy of the water increases. Second, the system releases some energy and it works on the environment (maybe heating the air around the water, making the air rise).

A Second Law

The big finish! The second law of thermodynamics explains that it is impossible to have a cyclic (repeating) process that converts heat completely into work. It is also impossible to have a process that transfers heat from cool objects to warm objects without using work.

In English: that first part of the law says no reaction is 100% efficient. Some amount of energy in a reaction is always lost to heat. Also, a system can not convert all of its energy to working energy.

The second part of the law is more obvious. A cold body can't heat up a warm body. Heat naturally wants to flow from warmer to cooler areas. Heat wants to flow and spread out to areas with less heat. If heat is going to move from cooler to warmer areas, it is going against what is “natural”, so the system must put in some work for it to happen.

A Closer Look at the First Law

Remember the first law of thermodynamics? It described the conservation of energy. When you have a system and it changes, there are four ways it can change its energy. We'll talk about those four ways of changing energy in this section.

Four Thermodynamic Systems

Adiabatic describes a system that changes with no transfer of heat in or out. If a system expands adiabatically, then the internal energy (heat) of the system usually decreases. This is because you did some work to expand the system, and that had to come from the heat energy of the system (since no heat energy can enter the system).

The second type of system is isovolumic. You can probably see the term 'volum' in there. Iso usually stands for constant. Put them together and you get a system that changes, but the volume stays constant. These types of changes do not produce any work on the environment.

The third type of system is isobaric. You've seen the prefix iso before, and the suffix baric refers to pressure. This system changes but keeps a constant pressure. All of the change is in the volume of gas in the system. As you blow air into a balloon, the volume will increase, but the pressure will stay the same. As energy is put into the system, temperature or volume may increase (or both), but there will be no increase in temperature.

The fourth type of system is isothermal. One last iso prefix, and the suffix is now thermal. We're talking about systems that change in every way but their temperature. You would say that these systems are in thermal equilibrium. You would see that the pressure and volume change. As energy is put in the system, the pressure or volume will increase (or both), but there will be no increase in temperature.

A Closer Look at the Second Law

We're going to talk about the second law of thermodynamics here. Scientists use a word called entropy to describe the degree of freedom (randomness) in a system. Remember, there are two words in thermodynamics: entropy, which talks about randomness, and enthalpy, which is a measure of the heat energy in a system. Big difference.

Heat flows from hot areas to cold, not the other way. If its energy is to flow from cold to hot, it needs additional energy. Heat is also conserved when energy transfer occurs. That conservation means that when you look at the energy of both systems at the beginning of the reaction and at the end, the total energy amounts are equal. Energy has moved from one area to another, but the total remains the same.

The second law also considers the entropy of a system. Entropy is a measure of the amount of disorder (chaos) in a system. A good rule of thumb is the more disorder you have, the more energy you have.

Forward and Backward

You might hear the term reversibility. Scientists use the term reversibility to describe systems that are in equilibrium with themselves and the environment around them. When a system is in equilibrium, any change that occurs in one direction is balanced by an equal change in the opposite direction. Reversibility means that effects can be reversed. This implies that the system is isolated (nothing is interfering, nothing entering or leaving). Overall, their effect and change on the system are zero.

Even at Equilibrium

So you've got a system at equilibrium. Look closely and you'll find certain qualities. You'll find that in these systems the heat transfer is due to temperature differences. You'll also discover that wild changes do not happen in an isolated system. To get big changes, you need energy. When you're at equilibrium, there is no gain or loss of energy. Lastly, you'll see that there is no friction involved in the system. If friction occurred, heat would be created and work would be needed to overcome the friction. That work would take energy out of the system.

Energy and Enthalpy

Enthalpy is a measure of heat in the system. They use the formula H = U + PV. H is the enthalpy value, U is the amount of internal energy, and P and V are pressure and volume of the system. This system works really well for gases.

Affecting Enthalpy

There are factors that affect the level of enthalpy in a system. The enthalpy is directly proportional to the amount of substance you have. Chances are if you have more of a substance, you have more energy. If you visualize on a large scale, you can compare the enthalpy in a glass of water to the enthalpy in the ocean. The ocean has more total energy.

The second thing to remember is that the value for H (enthalpy) changes sign when the reactions or values are reversed. When a reaction moves in one direction, the sign is positive. When a reaction moves in the opposite direction, the value is negative. (Note: When you have numbers only, the idea of direction (as in vectors, for example) is difficult to convey. With numbers, we convey direction by using signs. One way is "positive" and the opposite way is "negative"). When a system is in equilibrium the speed of forward reactions equals the speed of reverse reactions.

The third idea to remember is called Hess's Law. If a process happens in stages or steps, the enthalpic change for the overall (isolated) system can be figured out by adding the changes in enthalpy for each step. This recognizes that energy is conserved in an isolated system. Many reactions occur in steps. Only after looking at each step, and combining their effects, are you able to understand and measure the entire process.

Energy and Entropy

Entropy is a measure of the random activity in a system. The entropy of a system depends on your observations at one moment. How the system gets to that point doesn't matter at all. If it took a billion years and a million different reactions doesn't matter. Here and now is all that matters in entropy measurements.

When we say random, we mean energy that can't be used for any work. It's wild and untamed. Scientists use the formula (delta)S = (delta)Q /(delta)T. "S" is the entropy value, "Q" is the measure of heat, and "T" is the temperature of the system measured in Kelvin degrees. When we use the symbol delta, it stands for the change. Delta T would be the change in temperature (the original temperature subtracted from the final).

Affecting Entropy

Several factors affect the amount of entropy in a system. If you increase temperature, you increase entropy.

(1) More energy put into a system excites the molecules and the amount of random activity.

(2) As a gas expands in a system, entropy increases. This one is also easy to visualize. If an atom has more space to bounce around, it will bounce more. Gases and plasmas have large amounts of entropy when compared to liquids and solids.

(3) When a solid becomes a liquid, its entropy increases.

(4) When a liquid becomes a gas, its entropy increases. We just talked about this idea. If you give atoms more room to move around, they will move. You can also think about it in terms of energy put into a system. If you add energy to a solid, it can become a liquid. Liquids have more energy and entropy than solids.

(5) Any chemical reaction that increases the number of gas molecules also increases entropy. A chemical reaction that increases the number of gas molecules would be a reaction that pours energy into a system. More energy gives you greater entropy and randomness of the atoms.