

Chapter 16: Thermodynamics for the Truly Lazy



This picture shows the explosive eruption of Mt. Redoubt in Alaska in 1991. Leading volcanologists believe that if a volcanic event of this size occurred in New York City, that it would be really surprising to everybody who lived there.

<http://commons.wikimedia.org/wiki/File:MountRedoubtEruption.jpg>

Section 16.1: Energy – It’s Not Just Red Bull Anymore

You’re probably familiar with Red Bull and other energy drinks. These beverages, when consumed, turn otherwise normal human beings into raving lunatics who annoy everybody with stories about the time they went to Denny’s and *totally got an extra pancake because the waitress was flirting with me*. You know the type.

Anyhow, that’s not the type of energy we’re going to talk about in this chapter. It would be fun to do so, but then the Red Bull people would sue me and I’d have to fake my own death.¹

What’s Energy?

Energy is the ability of something to produce heat or to do work. For example, the gasoline in your car is able to produce heat (i.e. make the car hot) as well as do work (make the car roll). The two types of energy are **potential energy** (stored energy) and **kinetic energy** (energy of motion). To give you an example, an unfired bullet contains a lot of stored energy in the form of the chemical bonds holding the gunpowder together, and a fired bullet contains a lot of kinetic energy because the bullet itself is able to impart a great deal of force to the target. This example also shows that it’s possible to convert potential energy to kinetic energy. When this occurs, there’s no net loss or gain of energy – this principle is known as the **law of conservation of energy** (aka the first law of thermodynamics).

It’s pretty handy to figure out where energy is going during a process, and to do this we need some way of quantitatively measuring how much energy there is. The main unit of energy is the **joule (J)**.² One thousand joules is called a kilojoule (kJ).

Talkin’ Like a Scientist



Figure 16.1: Both heat and work deal with the transfer of energy. Heat is when energy moves around due to the motion of molecules (i.e. hot things give energy to colder things), while work is when energy moves around mechanically (i.e. a moving hammer can put a lot of energy into a squirrel. Former President Jimmy Carter didn’t do much work from a thermodynamics standpoint, as energy wasn’t moved from one place to another. Whether he did any work from a conventional definition is open to interpretation.

http://commons.wikimedia.org/wiki/File:Jimmy_Carter.jpg

¹ Again

² 1 joule is defined as a $(\text{kg} \times \text{m}^2)/\text{s}^2$, which is why we just call it a joule instead of all those other units. Other units of energy include calories (the energy needed to heat 1 gram of water by 1°C) and British Thermal Units (BTUs, the energy needed to heat one pound of water from 39° to 40°C). How about we just use the Joule instead of trying to remember these?

Energy Needed To Make Stuff Hot

Let's say that we want to heat up a piece of aluminum. Why we would want to do that is anybody's guess, but let's pretend that doing so is desirable in some way. What things do we need to know before we can figure out how much energy this will take? Take a minute to think about it. I'll wait.

If you said that it will take three things, you're right. If you didn't, here they are:

- How much aluminum there is. Obviously, it will take more energy to heat 500 grams of aluminum than it will take to heat 5 grams of aluminum.
- How much do we want to heat it? It's clear that it will take more energy to heat it by 200° than it will to heat it by 20°.
- How easy is it to heat? Some things heat up really easily (most metals, for example), while other things take a lot more energy to heat up by the same amount (as is the case with water).

To put this into an equation form, we'll say that the amount of energy needed to heat the water (called ΔH) is:

$$\Delta H = m C_p \Delta T$$

The terms in this equation are pretty simple. The mass of stuff you want to heat is denoted by the letter "m". The number of degrees we want to heat it is denoted by " ΔT ." And the measure of how easy it is to heat one gram of the material by 1° C is called the **heat capacity**, denoted by " C_p ".³

Let's say we want to figure out how much energy it takes to heat 25 grams of water by 45° C. Given that the heat capacity of water is 4.184 J/g°C, we find that:

$$\Delta H = (25 \text{ grams})(4.184 \text{ J/g}^\circ\text{C})(45^\circ \text{ C}) = 4,700 \text{ J}$$

A couple of handy tips about these problems:

- Significant figures are still something you need to worry about. So worry about them.
- Every compound has a different heat capacity, and this heat capacity is different for each state of matter. For example, liquid water has a heat capacity of 4.184 J/g°C, while ice has a heat capacity of 2.01 J/g°C.
- The term ΔH in this equation is sometimes replaced by the letter "q", so if your teacher does this, don't be shocked. It doesn't really make any difference.

³ This term is also known as the "specific heat" and the "specific heat capacity", depending on who you're talking to. These terms all mean the same thing – the amount of energy needed to heat 1 gram of something by 1° C.

The Bomb That Won't Get You Arrested

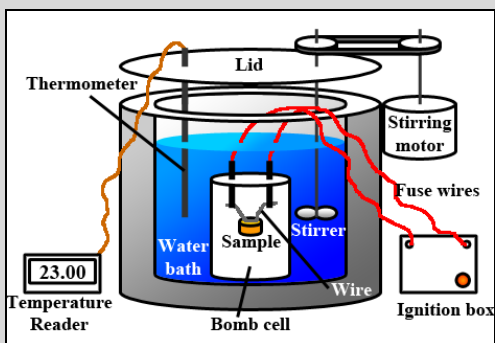


Figure 16.2: Sometimes it's handy to know how much heat is given off when a reaction occurs (known as ΔH_{rxn}). To do this, you perform a chemical reaction inside of a metal container that's immersed in water. Because all of the energy released by the reaction goes into heating the water, the equation $\Delta H_{rxn} = m C_p \Delta T$ can be used to figure out the heat of reaction from the mass of water in the container, the heat capacity of water, and the change in water temperature. This machine used to take these measurements is called a **bomb calorimeter**, and the metal cylinder where the reaction takes place is the **bomb**.

http://commons.wikimedia.org/wiki/File:Bomb_Calorimeter_Diagram.png

Section 16.2: Defining Thermodynamics

You've probably already guessed that we're talking about energy in this chapter. The study of energy is known as **thermodynamics**, which is a fun word to say and makes you sound smart.

One of the most important ideas in thermodynamics is the idea of system, surroundings, and universe. The **system** in a process is the thing that you actually care about. The **surroundings** consist of anything that interacts with the system, and the **universe** is equal to the system and its surroundings. For example, let's imagine a guy freezing to death in Greenland. To him, the system is his body (he cares about how much energy he has), the surroundings are the snow and ice around him (because they're pulling energy out of him), and the universe is a combination of the guy and his frozen surroundings.

The energy change in one system is the opposite of the energy change of its surroundings. If the freezing guy loses 1,000 J of energy from his body, the environment gains that 1,000 J.⁴

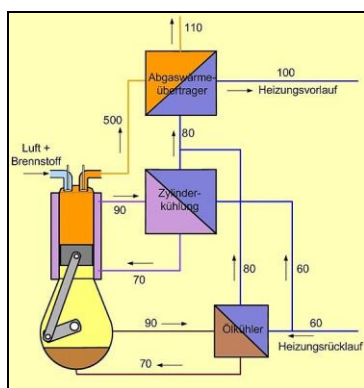


Figure 16.3: This picture has something to do with thermodynamics, but because I don't speak German I have no idea what. Let's just assume that it's somehow relevant to this section.

<http://commons.wikimedia.org/wiki/File:BHKW-Schaltplan.jpg>

⁴ That's the whole "law of conservation of energy" thing from earlier.

Enthalpy

As mentioned earlier, energy comes in two flavors: heat and work. Because reactions are usually performed in an environment where work isn't done (i.e. at constant atmospheric pressure, where nothing is mechanically moved), we usually just worry about the heat of a system. The heat that a system has under these conditions is called its **enthalpy (H)**.

That's the good news. The bad news is that there's no way to figure out how much heat a system has. After all, a hot piece of steel may look like it has a lot of heat when it's put into contact with a piece of ice, but will appear as if it has considerably less heat when you put it into a red-hot furnace. Because of this, it's impossible to know what the enthalpy of any system is.

We can, however, measure the change in heat for a process. You may not know how much heat a piece of hot steel has, but you can tell if you've added 1,000 J of energy to it because it will behave more energetically when you put it into contact with other systems. In our example above, it will either be able to melt more ice, or will not accept as much energy from a furnace.⁵

When a reaction causes the system to give off energy (i.e. it gets hot), it is said to be **exothermic** and ΔH for the reaction is negative – this denotes the loss of energy from the system. When a reaction absorbs energy (i.e. it gets cold), it is said to be **endothermic** and ΔH is positive – this is because the system has gained energy.

Focus on Real-Life Chemistry



Figure 16.4: One common example of an endothermic reaction occurs when you cook a puppy. Because the energy of the system / puppy increases as it is cooked, ΔH for the process is positive.

http://commons.wikimedia.org/wiki/File:Microwave_oven.jpg

⁵ Another example of how this works might be seen by imagining a large graduated cylinder with the bottom half full of rocks. If the water is up to the 900.0 mL level, you don't know how much water is actually in the cylinder because the rocks take up some of the volume. However, if you add water until the level reads 950.0 mL, you can be sure that, no matter how much water was in it before, there is now 50.0 mL more than there used to be.

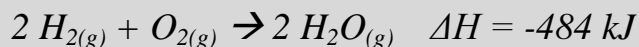
There are many different designations for enthalpy, depending on the process that you're trying to measure. These include the following:

- **Heat of reaction (ΔH_{rxn}):** This term refers to the amount of energy released or absorbed during a chemical reaction.
- **Heat of combustion (ΔH_{comb}):** This term refers to the amount of energy released when something burns.
- **Heat of solvation (ΔH_{solv}):** The amount of energy released or absorbed when one mole of something dissolves in water.
- **Standard heat of formation (ΔH_f°):** The amount of energy needed to make one mole of a compound from its elements in their standard states (i.e. their states at a temperature of 298 K / 25^o C and at a pressure of 1 atm).⁶
- **Molar heat of fusion (ΔH_f):** The amount of energy needed to melt one mole of a substance.
- **Molar heat of vaporization (ΔH_{vap}):** The amount of energy needed to boil one mole of a substance.

There are probably a bunch of other heats of [something] that I haven't heard of, but you probably don't need to worry about them.

Chemical Equations and You

Chemical equations in the world of thermodynamics are pretty much the same as any other chemical equation, except that they have a ΔH term after it to indicate how much energy is either released or absorbed during the reaction. For example, the complete equation for the reaction of hydrogen with oxygen to form water is:



Where the negative sign on ΔH indicates it is an exothermic reaction.

Section 16.3: Finding Enthalpies of Reaction

Let's say that you're doing a chemical reaction and don't, in the process, want to blow yourself up. To make sure this doesn't happen, it's good to know how much energy is going to be given off during a reaction, or how much will be absorbed. After all, a hugely exothermic reaction could really ruin your day.

There are a couple of ways to figure out ΔH for a reaction. As you can probably guess, you're going to learn them now.

⁶ Standard conditions for thermodynamics (298 K and 1 atm) are different than the standard temperature and pressure (STP) used in gas law problems (273 K and 1 atm). The reason for this is historical and not really of all that much interest, but make sure you don't confuse them.

Hess's Law

Here's the scenario: You know that you want to do a chemical reaction, but don't have any idea what the heat of reaction is. However, you do have a great big table with a whole bunch of other heats of reaction. How can we use this to our benefit?

This is where Hess's Law comes in. **Hess's law** states that, by adding or subtracting chemical reactions with the same products or reactants as the one you're interested in, you can figure out the overall heat of reaction that you're interested in.

Because the above statement doesn't really make all that much sense, let's use an analogy. Let's say that you're curious about how high a little town is above sea level. The problem, however, is that you don't have any way of measuring this. However, somebody has been nice enough to tell you the following information:

- The local mountain has an altitude of 3,500 feet above sea level.
- The altitude of the town is 800 feet lower than that of the mountain.

Seen this way, it's pretty easy to see that the town is $3,500 - 800 = 2,700$ feet above sea level. To figure this out, all we did was take existing data and reorganize it to figure out what we wanted. Pretty simple stuff, really.

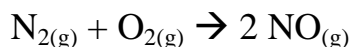


Figure 16.5: Annoying people on mountain bikes are often found showing off in mountain towns. They then go riding down the road, blocking traffic for normal people in cars. When I get mad, they're all "But we're saving the environment." News flash, dude: Your bike was made in a polluting factory. If you want to save the world so much, go for a walk and get out of the road. Jerk.

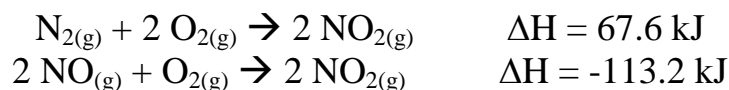
http://commons.wikimedia.org/wiki/File:Mountain_bike_cyclist_Chris_Clark_de_monstrates_a_maneuver.jpg

Likewise, we can do the same kind of thing with chemical reactions. If we don't know the heat of reaction for a process, but do know the heat of reaction for some related processes, with a little luck we'll be able to figure out what we want to know.

Let's see how this works: Imagine that I want to find ΔH_{rxn} for the process:



but all I know is the following information:



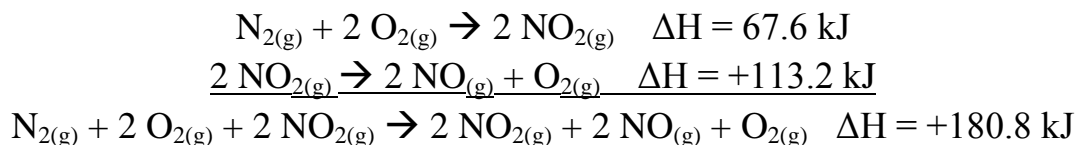
How do I solve this problem? Well, it turns out that if you can figure out the right way to add the equations you're given together, you can figure out the heat of reaction for the process you actually care about. The rules for doing this are simple:

- If you want to reverse the order of the products and the reactants, just change the sign of ΔH . For example, if you know that $A + B \rightarrow C$ has a ΔH of -100 kJ, then the reaction $C \rightarrow A + B$ will have a ΔH of $+100$ kJ.
- If you want to multiply the terms in the reaction together, also multiply your ΔH value. For the above example of $A + B \rightarrow C$, where $\Delta H = -100$ kJ, the reaction $2 A + 2 B \rightarrow 2 C$ will have a ΔH of -200 kJ.

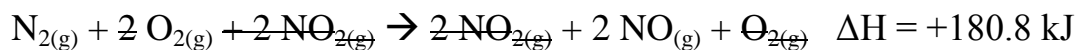
Given these handy rules, let's solve the $N_{2(g)} + O_{2(g)} \rightarrow 2 NO_{(g)}$ example from the last page. I'll walk you through what I did step by step, so you can see my reasoning:

- The first equation, $N_{2(g)} + 2 O_{2(g)} \rightarrow 2 NO_{2(g)}$, has one mole of N_2 on the reactants side, just like the reaction that we're trying to attain. This suggests to me that we not change anything and simply use it without making any changes. Thus, the equation we'll be using is simply $N_{2(g)} + 2 O_{2(g)} \rightarrow 2 NO_{2(g)}$, with a $\Delta H = 67.6$ kJ
- The second equation, $2 NO_{(g)} + O_{2(g)} \rightarrow 2 NO_{2(g)}$, has 2 moles of NO on the reactant side, while the reaction we want to find has 2 NO on the products side. This suggests to me that we should reverse the reaction to give us $2 NO_{2(g)} \rightarrow 2 NO_{(g)} + O_{2(g)}$, with a $\Delta H = +113.2$ kJ (the sign has been changed).

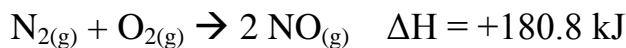
OK... now that we've manipulated both equations, let's add them together to see if we've done it right.



Because we can cancel out the terms that are present on both sides of the equation, we end up with:



which, when you get rid of the annoying crossed-out terms, gives us our answer:



Boring Men of Science



Figure 16.6: Hess's law was discovered by Germain Henri Hess, a Russian chemist who lived in the 19th century. Hess gets a special mention for being boring, because there's not one single fun fact about him to be found anywhere online. Seriously, check it out.

http://commons.wikimedia.org/wiki/File:Hess_Germain_Henri.jpg

Heats of Formation

Another way that you can find the heat of reaction is to use the standard heats of formation as your guide. To do this, use the following cool equation:

$$\Delta H_{\text{rxn}}^0 = \sum \Delta H_{\text{f}}^0(\text{products}) - \sum \Delta H_{\text{f}}^0(\text{reactants})$$

Of course, if you're a normal person, this equation makes no sense at all. What's the deal with all those terms?

Here's the scoop: Let's say that we have a great big bunch of standard heats of formation. If we've got the heats of formation for the compounds in our reaction, we can figure out the standard heat of reaction. This is done by adding up all of the heats of formation for the products, and then subtracting the heats of formation for the reactants. Let's see a simple example:

Let's say that we want to find the standard heat of reaction for the process $A + 2 B \rightarrow 3 C$, given the following information:

$$\Delta H_{\text{rxn}}^0(\text{A}) = -150.0 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}}^0(\text{B}) = 250.0 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}}^0(\text{C}) = 200.0 \text{ kJ/mol}$$

Given this, we can find the standard heat of formation in the following way:

- The sum of the standard heats of formation of the products in this reaction is equal to three times the standard heat of formation of compound C, or $3 \times 200.0 \text{ kJ} = 600.0 \text{ kJ}$.
- The sum of the standard heats of formation of the reactants in this reaction is equal to the standard heat of formation of A (-150.0 kJ) plus twice the standard heat of formation of B ($2 \times 250.0 \text{ kJ} = 500.0 \text{ kJ}$), which equals 350.0 kJ.
- The heats of formation of products minus the heats of formation of the reactants is equal to $600.0 \text{ kJ} - 350.0 \text{ kJ} = 250.0 \text{ kJ}$.

Which is awesome.

Irrelevant But Cool



Figure 16.7: HEAT isn't just for chemists – it's also an acronym for High Explosive Anti Tank weapons. Shown here is the FGM-148 Javelin anti-tank missile being fired by a member of the American armed forces.

<http://en.wikipedia.org/wiki/File:Javelin3.jpg>

Section 16.4: Spontaneity

Some reactions happen and some don't. You may have noticed that wood burns pretty well when you put a match to it, but that rocks don't seem to burn anywhere near as well. Which is a good thing, given that our planet is made of both rocks and very hot lava.

In any case, whether or not a reaction will occur on its own⁷ is referred to as **spontaneity**. Keep in mind that if a process is spontaneous, that doesn't necessarily mean that it happens quickly. For example, the combustion of the wood I mentioned above is a spontaneous process, but happens so slowly in the absence of heat that you'd never notice it.⁸

Spontaneity is measured by a value known as the **Gibbs free energy**, denoted by ΔG . If the Gibbs free energy for a process is negative, it will be spontaneous. If it's positive, it will be nonspontaneous. And if it's zero, it's an equilibrium process.⁹

Since it's nice to know if a process will spontaneously occur, we need to know how to calculate the Gibbs free energy of a process. Fortunately, the equation for ΔG is shown below:

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is our old friend enthalpy, T is the temperature in Kelvin, and ΔS is the change in entropy for the process.

Boring Men of Science

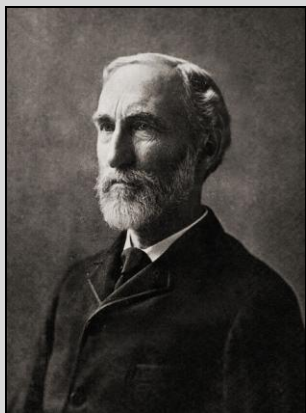


Figure 16.7: Gibbs free energy is named after Josiah Willard Gibbs, a 19th century scientist. Friends described him as having “no striking ways” and being “devoid of personal ambition.” However, they did praise his wardrobe, stating that he was “always neatly dressed” and “usually wore a felt hat on the street.”

http://en.wikipedia.org/wiki/File:Josiah_Willard_Gibbs_-_from_MMS-.jpg

What's entropy? Keep reading and find out!

⁷ i.e. without adding any energy to the system.

⁸ Thermodynamics describes whether something will give off or absorb energy during various processes. Kinetics is determines how fast these processes will occur. This is why a process can be thermodynamically “spontaneous” but still happen at an immeasurably low rate.

⁹ An equilibrium process is spontaneous in both directions. More about that in future chapters.

The Magic of Entropy

Entropy (denoted by S), to put it simply, is a measurement of the randomness of a system. Believe it or not, the randomness of a system is something that you can assign a specific energy to – the more random the particles in a system, the higher the value of the energy associated with this randomness.

To give you an idea of how energy is related to randomness, imagine throwing a handful of pennies that are all head side up at your teacher. When they bounce off of him/her and land on the floor, it's unlikely that all of them will be heads, or will be tails, for that matter. This is a quick demonstration of how systems tend to become more random on their own, given the opportunity.¹⁰



Figure 16.8: Comedian Andy Dick, shown here holding a piñata with a picture of Tom Green's head on it, is known for his erratic behavior. He is yet another example of how a system, when left to its own devices, tends toward randomness.

theonesecondfilm.com <http://www.flickr.com/photos/the1secondfilm/>

For a chemical process, how do we know whether the entropy increases or decreases? To find the change in entropy (ΔS) for a process, ask yourself a simple question: Do the molecules move around more or not? For those of you who don't like to ask yourselves simple questions, you can use the following guidelines:

- If you melt or boil something, entropy increases (ΔS is positive). This is because the particles go from moving a little bit to a whole lot more during these processes. Likewise, ΔS is negative when freezing or condensing a substance.
- If a reaction produces a gas, entropy increases (ΔS is positive). Gases are high entropy systems because the particles are moving around all over the place, so making a gas increases the entropy of a system. Note: If the reactants are also gases, the entropy will increase only if the number of gas molecules increases during the reaction, otherwise ΔS decreases.
- When solids dissolve, entropy increases (ΔS is positive). Consider this: When you dissolve sodium chloride in water, you go from a situation where the ions in the crystal are all locked in place to a situation where they're floating all over a solution.
- When gases dissolve in liquids, entropy decreases (ΔS is negative) – this is the case when carbon dioxide is dissolved in water when soda is made. Again: Carbon dioxide molecules go from flying all over the place (high entropy) to being stuck in solution (lower entropy).

¹⁰ This is, of course, a ridiculous oversimplification of how entropy works. However, it's the best I can do without getting into statistical thermodynamics. And believe me, you don't want to do that right now.

Is It Spontaneous?

Well, we've done all this talking about entropy and enthalpy, and we've even seen the equation for Gibbs free energy that tells us whether a process will be spontaneous. In case you forgot it, the equation is $\Delta G = \Delta H - T\Delta S$, and if ΔG is negative, the reaction is spontaneous.

The big question: What does this equation *really* mean, given what we know about thermodynamic stuff? The answer: When the energy of the system goes down (i.e. things become more stable), then things are more likely to be spontaneous. Let's have a look...

- If a reaction is exothermic, it's more likely to be spontaneous. If ΔH is negative, the first term in the equation above is negative, making it more likely that ΔG will be negative. In normal people terms, what this means is that if a system gives off a big bunch of energy as heat, this is a good thing.
- If a reaction causes an increase in randomness of the system¹¹, it's more likely to be spontaneous. If ΔS is positive, the $T\Delta S$ term in the equation is negative, which makes ΔG more likely to be negative, too. In normal people terms, it's a good thing when a system gets messier.

Put it all together, and you get the equation I've mentioned several times before:

$$\Delta G = \Delta H - T\Delta S$$

Let's do a sample calculation using this equation so that we can feel that we know what we're doing:

Question: If the heat of reaction for a process is -45.0 kJ and the entropy change for the process is 3.50 J/K, will the process be spontaneous or nonspontaneous at 298 K?

Answer: Let's plug these things in:

ΔH is -45.0 kJ, and ΔS is -0.0035 kJ/K (we need to convert this to kJ so that the units of energy are the same as that for ΔH). Plugging this in with a temperature of 298 K, we find that:

$$\begin{aligned}\Delta G &= -45.0 \text{ kJ} - (298 \text{ K})(-0.0035 \text{ kJ/K}) \\ &= -45.0 \text{ kJ} + 1.04 \text{ kJ} \\ &= -44.0 \text{ kJ}\end{aligned}$$

Because ΔG is negative, this process is spontaneous at 298 K.¹²

¹¹ This is related to the second law of thermodynamics, which states that, for any process, the entropy of the universe must increase. Note that this doesn't say that the entropy of the system must increase, only that the total entropy of the system + surroundings has to go up.

¹² A reaction may be spontaneous at some temperatures and nonspontaneous at others. For example, in this problem, the reaction will become nonspontaneous at high temperature, as this will increase the $T\Delta S$ term in the equation. In this case, the temperature will be 12,900 K, which is a temperature much higher than you're ever likely to run into.

Making People Angry

There's an idea among creationists that evolution violates the second law of thermodynamics. After all, if you start off with a bunch of prehistoric goo sitting around on the face of the earth, the emergence of complex life is definitely a decrease in randomness/entropy for our planet. What's up with that? (<http://carm.org/second-law-thermodynamics-and-evolution>).

The problem with this thinking is that the Earth is not an isolated system. Though the emergence of life results in a decrease of Earth's entropy, the amount of energy that's been pumped into the Earth from the sun (and the corresponding increase in entropy of the sun) more than makes up for it. Whether or not you believe in evolution, you simply cannot use the second law of thermodynamics to disprove it.