ENTROPY AND THE SECOND LAW OF THERMODYNAMICS:

............How the universe works

The first law of thermodynamics is simply a statement of energy conservation. That is, it states that energy can always be accounted for, that the energy of the universe is a constant - it can be transferred between objects and can change form, but the total doesn't change. But the first law does not preclude things occuring that we know do not occur: A glass of water does not spontaneously separate into ice cubes and warm water even though the energy balance equations used in calorimetry problems would allow it. That is, energy conservation - the first law of thermodynamics - would allow for the possibility that a system in thermal equilibrium could separate into two systems - one at a higher temperature than the other - and that temperature difference could then be used to drive a heat engine to do work. The second law of thermodynamics explains why the universe does not work that way. It articulates the underlying principle that gives the direction of heat flow in any thermal process. The result, of course, fits our everyday experience. The second law states the reason why it is true.

> ***Heat naturally flows from higher temperatures to lower temperatures.***
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> ***No natural process has as its sole result the transfer of heat from a cooler to a warmer object.***
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> ***No process can convert heat absorbed from a reservoir at one temperature directly into work without also rejecting heat to a cooler reservoir. That is, no heat engine is 100% efficient.***

Carnot Cycle - Maximum Thermodynamic Efficiency in a Cyclic Process

It was observed by Sadi Carnot - a French scientist and engineer trying to

improve the efficiency of steam engines in the mid-1800s - that there is always waste heat rejected by a heat engine. And that waste heat limits the efficiency of the engine since energy has to be conserved or accounted for. In trying to understand the limits of efficiency, he stated that in any heat engine in principle there would always be rejected heat (even in an ideal engine) - and the net work done would be the difference between the heat absorbed and that rejected. He then set out to determine the principles that would affect that efficiency. He stated that the most efficient heat engine possible would be one that worked reversibly - an ideal that could never be attained. This would mean that heat transferred into or out of the system (the heat engine) would only occur at constant temperatures - the high or the low temperatures between which the heat engine operated. That is, the system would stay at the temperatures of the reservoirs during those heat transfers - necessary for the process to be reversible since the heat flow could not be reversed to go from the lower to the higher temperature. And furthermore, said Carnot, the maximum conceivable efficiency would be limited by those two temperatures. The most efficient thermodynamic cycle operated between any two temperatures is therefore called a *Carnot cycle*.

The Carnot cycle is a four step process involving two isothermal processes (which are said to be ideal reversible processes) at the temperatures Th and Tc and two adiabatic processes (ie, without heat transfer) which operate between those two temperatures. In the isothermal steps, there is no change in internal energy and the heat exchanged is equal to the work done. In the two adiabatic processes, there is no heat exchanged. No such system can ever be built - since it is an idealized process (the two isothermal steps being reversible and quasistatic which means, in effect, they occur infinitely slowly). The importance of the process is that it gives an upper limit to the efficiency of any cyclic process between the same two temperatures.

Entropy and the Second Law of Thermodynamics

In trying to synthesize the ideas of Kelvin, Joule, and Carnot - that is, that energy is conserved in thermodynamic processes and that heat always "flows downhill" in temperature - Rudolf Clausius invented the idea of *entropy* in such a way that the change in entropy is the ratio of the heat exchanged in any process and the absolute temperature at which that heat is exchanged. That is, he defined the change in entropy DS of an object which either absorbs or gives off heat Q at some temperature T as simply the ratio Q/T.

With this new concept, he was able to put the idea that heat will always flow from the higher to the lower temperature into a mathematical framework. If a quantity of heat Q flows naturally from a higher temperature object to a lower temperature object - something that we always observe, the entropy gained by the cooler object during the transfer is greater than the entropy lost by the warmer one since Q/Tc.>|Q|/Th. So he could state that the principle that drives all natural thermodynamic processes is that the effect of any heat transfer is a net increase in the combined entropy of the two objects. And that new principle establishes the direction that natural processes proceed. All natural processes occur in such a way that the total entropy of the universe increases. The only heat transfer that could occur and leave the entropy of the universe unchanged is one that occurs between two objects which are at the same temperature - but that is not possible, since no heat would transfer. So a reversible isothermal heat transfer that would leave the entropy of the universe constant is just an idealization - and hence could not occur. All other processes - meaning, all *real* processes - have the effect of increasing the entropy of the universe. That is the second law of thermodynamics.

Entropy is a measure of the disorder of a system. That disorder can be represented in terms of energy that is not available to be used. Natural processes will always proceed in the direction that increases the disorder of a system. When two objects are at different temperatures, the combined systems represent a higher sense of order than when they are in equilibrium with each other. The sense of order is associated with the atoms of system A and the atoms of system B being separated by average energy per atom - those of A being the higher energy atoms if system A is at a higher temperature. When they are put in thermal contact, energy flows from the higher average energy system to the lower average energy system to make the energy of the combined system more uniformly distributed - ie, less ordered. So the disorder of the system has increased - and we say the entropy has increased. But the process of increasing the disorder has removed the possibility that the energy that was transferred from A to B can be used for any other purpose - for example, work cannot be extracted from the energy by operating a heat engine between the two reservoirs of different temperatures. So although energy was conserved in the transfer (the first law), the entropy of the universe has increased in becoming more

disordered (the second law) and consequently the availability of energy for doing work has decreased.

The second law of thermodynamics can be summarized in many different statements - and has been by many thermodynamicists in the last century and a half. All of the statements are an attempt to put a reason to the things all of us have observed - that when two objects are in thermal contact, heat always goes from the warmer to the cooler and never the other way. This universal result has probably as many explanations as there are physicists trying to explain it - and is still the subject of serious consideration by some of the best theorists. The difficulty does not lie in what the second law says - or how it should be interpreted - but rather in what the fundamental, underlying reason is for why nature behaves in that way.

> ***Any process either increases the entropy of the universe - or leaves it unchanged. Entropy is constant only in reversible processes which occur in equilibrium. All natural processes are irreversible.***
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> ***All natural processes tend toward increasing disorder. And although energy is conserved, its availability is decreased.***
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> ***Nature proceeds from the simple to the complex, from the orderly to the disorderly, from low entropy to high entropy.***
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> ***The entropy of a system is proportional to the logarithm of the probability of that particular configuration of the system occuring. The more highly ordered the configuration of a system, the less likely it is to occur naturally - hence the lower its entropy.***

In the language of entropy, the Carnot cycle still represents the theoretical maximum efficiency in any cyclic process. That is, maximum efficiency would occur if the entropy of the universe did not increase, hence there would be no loss of availability of doing work. But entropy can only remain constant in a reversible isothermal process. So, again, any heat transfer

would have to occur isothermally. Therefore the most efficient cyclic process possible involves only reversible isothermal steps and steps in which no heat is transferred - ie, adiabatic. And even in this idealized reversible process in which the entropy of the universe was left unchanged, the efficiency of conversion of heat to work is limited by the two temperatures involved in the isothermal steps.

Based on the ideas of Lord Kelvin, Joule, Boltzmann, Carnot, and Clausius, the first and second laws of thermodynamics can now be restated in two profound sentences:

> **The total energy of the universe is a constant.**
>
> **The total entropy of the universe always increases.**

And these two fundamental principles of nature describe how the universe works.