The Unbreakable Law

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One essential skill of an expert witness is to modify the brains of those involved in a dispute (lawyers, arbitrators, judges) so that they understand highly technical issues which they would normally not understand. It's also an essential skill of teachers and those investigating incidents. I've performed all of these roles.

I struggled to deeply understand Entropy for years. Entropy arises from the Second Law of Thermodynamics. This law can be stated in various ways but the simplest for our purpose is that heat cannot flow from a cold object to a hot object unless work is done. The implications that arise from this are massive. Entropy is a thermodynamic property which is involved in every process in the Universe, from mechanical and electrical work, chemical and biological processes to black holes and stars. The Second Law is regarded as impossible to break. It predicts how the Universe is likely to end. It can explain why time runs in one direction, that of constantly increasing Entropy of the Universe. To reverse the direction of time requires the Entropy of the Universe to decrease.

If you can read this short article (possibly more than once) and afterwards understand Entropy, I will have succeeded in modifying your brain to understand a difficult concept. I'm an Engineer not a physics graduate but I can learn something new with sufficient mental clarity to be able to explain it to someone else.

I must start with some definitions.

The temperature of something is commonly measured by the Celsius (Centigrade) scale, where water freezes at 0° C and boils at 100° C. In some places, the Fahrenheit scale is used, where water freezes at 32° F and boils at 212° F. Daniel Fahrenheit wanted to avoid negative numbers in his temperature scale, so he set 0° F as the lowest stable temperature he could create with a mixture of brine and ice. 100° F is slightly warmer than Daniel's armpit. In the Centigrade scale, there are 100 degrees between freezing and boiling water. In Fahrenheit's scale, there are 180 degrees between freezing and boiling water.

In physics, a different temperature scale is used. The Kelvin scale sets 0 degrees at absolute zero – the temperature at which molecules have no thermal energy. Gas molecules would stop moving. Kelvin uses the same sized degrees as the Celsius scale. Water freezes at 273 K and boils at 373 K. Note that a Kelvin temperature is denoted by the letter K, without a ° symbol. To convert a temperature in °C to K, add 273.

All work done can be expressed in terms of raising a weight by a height (force x distance). The unit of work is the Joule. If a weight of 1 kg is lifted by 1 metre, this takes 9.81 Joules of work. One Joule is also the work involved if one watt of electrical power operates for one second. If you set your microwave at 1000 watts (1 kW) for one minute to heat up a cooled mug of coffee, the work involved is 1000 x 60 = 60,000 Joules. To heat one litre of water by 1° C takes 4,186 Joules of energy.

Thermodynamics considers a System as distinct from the Surroundings, which are the rest of the Universe. A System is a volume which is defined by the boundary we choose to consider, depending on what we want to analyse. A boundary is a defined surface that separates the System from the Surroundings.

There are 3 different types of boundary:

1) **An Isolated system.** This has a rigid boundary that is perfectly insulated. No energy or matter can cross the boundary. Think of a perfectly insulated, sealed Thermos flask.

2) **A Closed system.** Energy can cross but not matter. The boundary doesn't have to be rigid. Think of the refrigerator in your kitchen with the door closed. Energy (heat) can cross because it's not a perfect insulator. Matter cannot cross because the door is sealed. A piston in the cylinder of an engine with the valves closed is another example.

3) **An Open system.** Energy and matter can cross the boundary. Think of a turbine engine or the walls of a cell in your body.

Entropy is a measure of how energy is dispersed within a system. At maximum Entropy, energy is uniformly distributed throughout the system. The units of Entropy are Joules per degree Kelvin.

There are two important ways in which Entropy can be analysed; Thermodynamic and Statistical. Each gives important insights.

Thermodynamic Entropy analysis

The **change** in entropy of a System or the Surroundings is calculated by dividing the Joules of energy lost or gained by the Kelvin temperature of the System or Surroudings under consideration. I'll use 6 decimal places in the calculations below to show small differences.

A quick calculation will show how the transfer of heat affects the Entropy of a System and the Surroundings. Consider a refrigerator as a Closed System with an internal temperature of 4^o C (the "Cold reservoir"). This equals 277 K (adding 4^o C + 273). The temperature outside the refrigerator is at 20^o C (293 K) (the "Hot reservoir"). The power is cut, the compressor stops working and heat energy leaks from outside the refrigerator to the inside. 1000 Joules of heat moves from the Surroundings to the System.

The Entropy inside the refrigerator changes by +1000 J (positive because heat is added) at a temperature of 277 K. The change in Entropy is 1000 J ÷ 277 K = +3.610108 J/K.

The Entropy of the Surroundings changes by -1000 J (negative because heat leaves) at a temperature of 293 K. The change in Entropy is -1000 J ÷ 293 K = -3.412969 J/K.

If we add these changes together, the overall change in Entropy of the System and the Surroundings is +3.610108 – 3.412969 = +0.197139 J/K. **The Entropy of the Universe has increased by 0.197139 J/K.**

When a transfer of heat takes place between a System and the Surroundings which causes an overall increase in Entropy and requires no external work, that process is called "Spontaneous". A Spontaneous thermodynamic process is one that takes place without work having to be performed. You can think of it as something that will take place naturally but which is not naturally reversible, such as an ice cube melting. It is impossible for the water to turn back into an ice cube without some work being done to achieve that. The warming refrigerator is a Spontaneous process.

Now the power comes back on. The compressor starts to work again and 1000 J of heat energy is transferred out of the cold System and into the warm Surroundings. At first view, the overall Entropy seems to decrease by the same amount as it increased; 1000 Joules of heat energy is transferred from inside the fridge at 277 K to the surroundings at 293 K giving an overall Entropy change (decrease) of -0.197139 J/K.

However work must be done by the compressor to cause this non-Spontaneous heat transfer, which adds more heat and Entropy to the Surroundings. We must calculate the total amount of energy put into the surroundings and the resulting increase in Entropy. Then we can subtract the Entropy decrease inside the System from the Entropy increase in the Surroundings.

The refrigeration system to cool the inside of the refrigerator needs an input of energy to work. The Cold Reservoir (inside the refrigerator) is at 277 K and the Hot Reservoir (Surroundings) is at 293 K. How much energy is required to drive the refrigerator? We use the formula to find the Coefficient Of Performance (COP) for a refrigerator.

$$COP = T_{\text{Cold Reservoir}} \div (T_{\text{Hot reservoir}} - T_{\text{Cold Reservoir}}) = 277 \div 16 = 17.31$$

The **theoretical minimum work** required to move 1000 J out of the fridge is 1000 J ÷ 17.31 = 57.77 J.

In a refrigerator, the electrical work goes into the motor/compressor as mechanical work, but in steady operation it all ends up as heat dumped to the surroundings. This adds 57.77 J of energy as heat to the surroundings.

To drive the compressor requires power. Let’s take a look at the power station. The maximum possible efficiency of a heat engine is found using the formula given by a young French engineer, Sadi Carnot. He gave us this simple formula for a heat engine:

$$\text{Maximum possible efficiency} = 1 - (T_{\text{sink}} \div T_{\text{source}})$$

T_{sink} is the temperature of the Surroundings.

T_{source} is the temperature of fluid fed into the System.

If a power station feeds superheated steam at 573 K to drive a turbine (System) with a Surroundings (T_{sink}) temperature of 293 K, the calculation shows:

$$\text{Maximum possible efficiency} = 1 - (293 / 573) = 1 - 0.51 = 0.49$$

This means that of the power input into the turbine, 49% leaves as electricity and 51% goes to the surroundings as heat. Even with no other source of inefficiency (heat loss through the engine cooling system, friction in bearings etc), to produce 57.77 J of energy to the compressor requires 57.77 ÷ 0.49 = 117.83 J input energy. This means that 117.83 – 57.77 = 60.13 J (51% of the total input energy) enters the surroundings from the turbine as heat.

System (refrigerator) Entropy decrease = -1000 J ÷ 277 K = -3.61 J/K

Total Surroundings energy increase = 1000 + 57.7 + 60.13 = 1117.83 J

Surroundings Entropy increase = 1117.83 J ÷ 293 K = 3.82 J/K

The theoretical minimum possible increase in Entropy of the Surroundings is 3.82 J/K. In reality there is also heat loss through the electricity transmission system, through friction within the turbine and other losses which mean that the turbine must output even more energy for 57.77 J to reach the compressor.

Net Entropy increase = 3.82 – 3.61 = 0.21 J/K

To move 1000 J of heat from the refrigerator to the Surroundings causes an increase in the entropy of the Universe, dominated by Entropy production at the power station. The Spontaneous transfer of heat from the warm Surroundings to the cold System and the non-Spontaneous transfer of heat from the cold System to the warm Surroundings have both increased the total Entropy of the Universe.

Note that whether a process is spontaneous or not, during the course of any process the Entropy of the Universe increases.

Any process giving work requires some difference in energy levels to operate. More pressure on one side of a piston than the other side, higher vs lower temperature or concentration of chemicals or magnetic flux or electrical potential. When there is no difference in energy levels in different places within a System and everything is in equilibrium, Entropy is maximum and no process providing work is possible. No chemical reactions, no movement, no life.

I said earlier that Entropy is a measure of how energy is dispersed within a System. Imagine that your kitchen is an Isolated System and we imagine that the Boundary is perfectly sealed and insulated. No energy or matter can cross the boundary. In order to keep the refrigerator cool, a battery pack inside the System provides power to the compressor. Entropy within the Surroundings increases because the non-Spontaneous work of the refrigeration system moving heat from the refrigerator to the room causes an overall increase. When the battery pack runs out of power, the compressor stops. Heat starts to move from the room into the refrigerator, Entropy increases within the refrigerator. Eventually, the temperature inside and outside the refrigerator become the same. Transfer of energy stops. Energy is uniformly distributed within the System. Entropy has reached its maximum value. No further process is possible.

Some physicists think that over the next 10^{100} years (1 with 100 zeros, also called a Googol) the Universe will continue to expand, stars will burn out and eventually the Entropy of the Universe will reach its maximum. No more processes will be possible, no life will exist.

Statistical Entropy analysis

There is another way to analyse Entropy which gives additional insight. Think of a container filled with air. The pressure and temperature can be measured. These measurements show the large scale “Macro state” of the gas. If nothing changes and repeat measurements are made an hour later, the same values will result.

The molecules of gas constantly move around. The effect of these moving molecules colliding with the boundary gives rise to pressure. Their positions constantly change. The number of different possible arrangements of the positions of all the molecules is huge. Each of these possible arrangements is called a “Microstate”. Entropy counts the number of Microscopic arrangements that the System can have to give the same Macroscopic properties.

The air comprises 80% Nitrogen and 20% Oxygen. Reducing the possible number of Microstates reduces the Entropy. Imagine that the cylinder now has an internal wall which separates the Oxygen and Nitrogen molecules. The Entropy is less because the possible number of Microstates is less.

The Austrian physicist Ludwig Boltzmann gave us the relationship between absolute Entropy (symbol S) and the number of possible microstates in a System. His formula (which is carved on his gravestone in Vienna's central cemetery) is

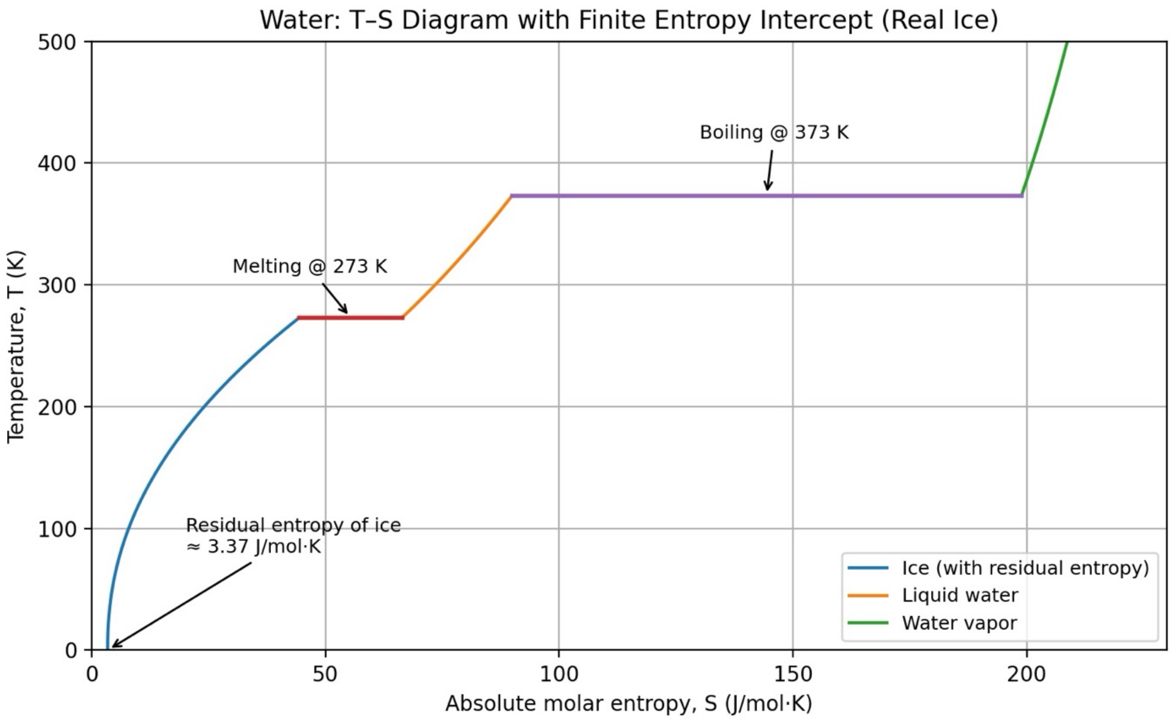
$$S = k_B \log W$$

k_B is the Boltzmann constant, which is effectively a conversion factor for using the Kelvin temperature scale. Its value is 1.380649×10^{-23} J/K. That's 0.000 000 000 000 000 000 000 0013 806 49.

An important insight is whether the number of possible Microstates is as big as is possible for the Macrostate, in which case Entropy is also at a maximum.

A perfect diamond crystal at 0 K has one Microstate. Each Carbon atom is in a fixed position within the crystal and there is only one possible lattice arrangement. At absolute zero, there is no thermal motion or vibration. For a perfect diamond crystal at 0 K with a single microstate, the number of possible microstates W = 1 and the logarithm of 1 is 0 so Entropy S = k_B x 0 = 0. As the diamond warms up, the atoms start to vibrate so there is no longer a single possible microstate. Entropy increases.

The water molecule H_2O is slightly boomerang shaped. Fixed within ice, the molecules can be orientated in different ways and so at 0 K, there are many possible microstates for ice and Entropy is not zero. If Entropy and temperature are plotted on a graph between 0 and 500 K, this is how it looks:



Graph of S vs T for 1 mol H_2O from 0–500 K with phase-change steps

During phase changes moving from ice to water and water to steam, energy is required to make that phase change. Entropy increases even though the temperature does not as additional energy creates more movement of the molecules and more possible microstates. The residual Entropy of water at 0 K is approximately 3.37 J/mol-K. This is the residual Entropy of one mole ($6.022\ 140\ 76 \times 10^{23}$ particles) of water molecules.

I hope that I succeeded in modifying your brain and that you enjoyed the process. Merry Xmas 2025.