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Entropy and the Second Law of Thermodynamics

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Overview:

The second law of thermodynamics is a fundamental law of nature. It states that the entropy of a system always increases over time, or remains constant in ideal cases where a system is in a steady state, or undergoing a "reversible process". If the system is undergoing an irreversible process, the entropy of the system will always increase. This means the change in entropy, ΔS, is always greater than or equal to zero. The entropy of a system is a measure of the number of microscopic configurations the system can attain. For example, gas in a container with known volume, pressure and temperature can have an enormous number of possible configurations of the individual gas molecules. If the container is opened, the gas molecules escape and the number of configurations increases dramatically, essentially approaching infinity. When the container is opened the entropy is said to increase. Therefore entropy can be considered a measure of the "disorder" of a system.

Commented [Amy Manoc1]: What about if an irreversible process occurs? Entropy always increases when an irreversible process occurs in a closed system.

Also, what about the fact that delta S is always greater than or equal to zero?

Principles of Entropy:

Entropy is a "state property", which is a quantity that depends only on the current state of the system. Quantities that are state properties do not depend on the path by which the system arrived at its present state. Therefore the most useful way to quantify a state property is to measure its *change.*
The change in entropy S is defined as

Commented [Amy Manoc2]: Why is change in entropy used? Ie. Why can't you measure a set value of entropy in an experiment? What is a state property?

$$\Delta S = Q / T, \quad \textbf{(Equation 1)}$$

where Q is the heat supplied to the system, and T is the temperature of the system. In the context of thermodynamics, heat, like work, is defined as a transfer of energy. Heat is energy transferred from one object to another because of a difference in temperature. Consider a bath of ice and water at 0^0 C. If one supplies heat to the ice/water bath, some of the ice will melt and the number of states available to the water molecules will increase by a large amount, proportional to the amount of heat that was added to the system. The entropy will then increase proportional to this amount. The relationship between two objects at different temperatures was first described by Newton.

Commented [Amy Manoc3]: Please introduce the concept of heat- this may be the first time the student sees this concept.

Newton's law of cooling states that the rate of change of the temperature of some object is proportional to the difference between its own temperature and the temperature of its surroundings. For an object at temperature T placed in a closed system at temperature T_f, this change in temperature as a function of time t is described by the differential equation:

$$dT/dt = -k(T - T_f) \quad \textbf{(Equation 2)}$$

where k is a constant that depends on the characteristics of the object and its surroundings. **Equation 1** is equivalently written as

$$-k\, dt = dT / (T - T_f). \quad \textbf{(Equation 3)}$$

Integrating both sides, this becomes

$$-k\, t = \log(T - T_f) + \log C. \quad \textbf{(Equation 4)}$$

Apply the exponential function to both sides of the equation, and rearrange to get

$$T - T_f = C\, e^{-kt}\ .\ \textbf{(Equation 5)}$$

If the object in question is at an initial temperature T_i at time $t = 0$

$$T_i - T_f = C.\ \ \textbf{(Equation 6)}$$

It follows that the temperature as a function of time is then

$$T(t) = T_f + (T_i - T_f)\, e^{-kt}\ .\ \textbf{(Equation 7)}$$

So when a hot object is placed in a cooler closed system, its temperature will decrease at an exponential rate. In this closed system, the heat from the hot object Q will increase the temperature of the cooler surroundings and thus increase the number of available states. Thus the change in entropy ΔS is positive and nonzero.

Commented [Amy Manoc4]: How does this then tie back in to the general topic of Entropy?

Procedure:

Commented [Amy Manoc5]: It would also be helpful to observe the increase in temperature of the ice bath over time. Then you can relate the transfer of heat between the hot and cold reservoir.

How much heat is transferred between the hot and cold reservoirs? What is Q? Then you can figure out what delta S is.

1. Observe Newton's Law of Cooling and measure the cooling constant *k.* Demonstrate the second law of thermodynamics

   1.1. Obtain a sample of lead with a slot for a thermometer to be inserted, a beaker large enough to hold the lead sample, a heating element, two ~~a~~ thermometers, a stopwatch, a rod attached to stand with clamps, a large bag of ice, water, and a container large enough to hold the lead sample and ice/water mixture.

   1.2. Fill the beaker with enough water that ~~your~~ the lead sample can be completely submerged without touching the bottom.

   1.3. Place the beaker of water on the heating element and turn it on. Heat the water until it reaches a boil.

   1.4. Attach the string to the lead sample so it can be suspended into the boiling water.

   1.5. Attach the thermometer and string to the clamp/rod so the bottom of the thermometer and the lead sample are suspended at the same height.

   1.6. Submerge the thermometer/lead sample into the boiling water until the sample is completely covered with water, but not touching the bottom. There may be a temperature gradient in the water beaker since the heating element is inputing a large amount of energy from the bottom of the beaker.

   1.7. Wait a few minutes for the sample to come to thermal equilibrium with the boiling water. Once ~~you think~~ they are in thermal equilibrium, record the temperature on the thermometer in **Table 1.**

1.8. Prepare the ice/water bath by filling it with the ice and water so there is enough to completely cover the lead sample.

~~1.8.~~ 1.9. Insert one thermometer in the ice bath and record the temperature in **Table 1.**

~~1.9.~~ 1.10. Remove the sample from the boiling water, insert the thermometer in the slot within the sample, and submerge in the ice/water bath. Immediately start recording the time with the stopwatch once the lead sample is submerged in the ice/water bath.

~~1.10.~~ 1.11. Record the temperature of the ice bath and lead sample simultaneously with the time as frequently as you can. Perhaps every minute for 30 minutes, then every 5 minute for the next 20 minutes. The time and temperature measurements need to be recorded at the same time. Record these values in **Table 1.** If at any point a large portion of the ice begins to melt, add more to the ice/water bath so the temperature remains at 0^o C.

~~1.11.~~ 1.12. After some time the temperature of the lead sample will reach that of the ice/water bath. At this point there is enough data and no more measurements need to be taken.

~~1.12.~~ 1.13. Plot the data points that were collected in **Table 1** in a graph of temperature versus time.

~~1.13.~~ 1.14. Using the initial temperature of the lead, the temperature of the ice/water bath, and any two data points for the time and temperature, solve **Equation 7** for the cooling constant *k.*

~~1.14.~~ 1.15. Using this value for *k,* plot the **Equation 7** as a continuous function in *t,* and compare that function with the data points that were collected.

Representative Results

Representative results for a 100^o C lead sample placed in an ice/water bath are shown in **Table 1.** The cooling constant k is found by the data points in the table and solving **Equation 7**. After 10 minutes it is known that $T(10) = 58$:

$$58 = 100\, e^{-k\, 10} \quad \textbf{(Equation 8)}$$

Solving for k one finds that $k = 0.054$. The curve with this cooling constant is shown as a dashed gray line in **Figure 1**, along with the data points from the experiment. It can be seen that the functional form of **Equation 6** matches the experimental results very closely.

The entropy of the lead + ice/water bath has increased, since much of the ice has melted. The number of states that the now melted water can occupy is much higher than it was before the lead was added to the bath.

The total change in entropy, ΔS_{tot}, is the sum of the individual changes in entropy of the lead sample and the ice/water bath:

$$\Delta S_{tot} = \Delta S_{lead} + \Delta S_{bath} \quad \textbf{(Equation 9).}$$

In differential form, the heat dQ added to the system can be calculated using the relationship between mass, specific heat c, and change in temperature:

$$dQ = mc\,dT. \quad \textbf{(Equation 10)}$$

where c is known to be 0.128 J/(g K) for lead. The total change in entropy is then

$$\Delta S_{tot} = \int_{T_{lead}}^{T_{final}} c_{lead}\frac{dT}{T} + \int_{T_{bath}}^{T_{final}} c_{water}\frac{dT}{T}$$

$$= c_{lead}\ln(T_{final} / T_{lead}) + c_{water}(T_{final} / T_{water}). \quad \textbf{(Equation 11)}$$

Using the conversion to Kelvin as K = C° + 273.15, the total change in entropy of the system is calculated as

$$\Delta S_{tot} = 0.128*\ln[(5 + 273.15)/(100 + 273.15)] + 4.18*\ln[(5+273.15)/273.15] \text{ J/K}$$
$$= 0.038 \text{ J/K.}$$

Time (min)	Leat Temp~~erature~~ (C°)	Ice/water bath Temp (C°)
0	100	0
1	94	0
2	89	1
3	74	1
4	79	1
5	78	1
6	72	2
7	69	2
8	64	2
9	62	2
10	58	3
11	56	3
12	53	3
13	49	3
14	47	3
15	45	3
16	43	3
17	41	3
18	37	4

Commented [Amy Manoc6]: So what is the value of delta S? How does the data prove that entropy increased?

19	35	4
20	34	4
21	30	4
22	30	4
23	28	4
24	26	4
25	26	4
26	25	4
27	23	4
28	21	4
29	19	4
30	19	4
35	14	4
40	10	5
45	8	5
50	5	5

Insert Figure 1

Summary:

Newton's law of cooling was observed by placing a lead bar at 100° C into a ice/water bath, and the entropy of the system was seen to increase. By measuring the temperature of the bar as a function of time over the period of 50 minutes, it was confirmed that the cooling of the bar is exponential in form. The cooling constant of lead was found by solving the cooling equation using collected data.

Applications

A pair of headphones that you keep in your bag always has a tendency to become knotted – this is an increase in entropy from carrying the bag around. One needs to do work on the headphones to un-knot them and decrease the entropy (this can be thought of as a "reversible process"). ~~A person's room or office doesn't stay clean on its own. Unless work is done on the room or office, the papers and books, after being read and referred to, will inevitably end up disordered. For a more morbid example, Newton's law of cooling is used by forensics teams to approximate how long a victim of a crime has been dead. They measure the temperature of the body when it is found, and knowing the average temperature of the human body and the average room temperature of the body, they can find the cooling constant *k* and subsequently find the time *t*.~~ The most efficient heat engine cycle is the Carnot cycle, which is the most efficient heat engine cycle allowed by physical laws. The second law states that not all heat supplied to a heat engine can be used to do work, the Carnot efficiency sets the limiting value on the fraction of heat which can be used. The cycle consists of two isothermal processes followed by two adiabatic processes. ~~.~~A refrigerator, which is essentially just a heat pump, is also a classic example of the second law. Refrigerators move heat from one location (the "source") at a lower

Commented [Amy Manoc7]: Classic applications of the second law of thermodynamics are refrigeration and the Carnot and Stirling engines. Could you add a bit about these types of applications? The examples given here are more basic descriptions of disorder, and don't relate to thermodynamics.

temperature to another location (the "heat sink") at a higher temperature, using mechanical work. According to the second law, heat cannot spontaneously flow from a colder location to a hotter one,

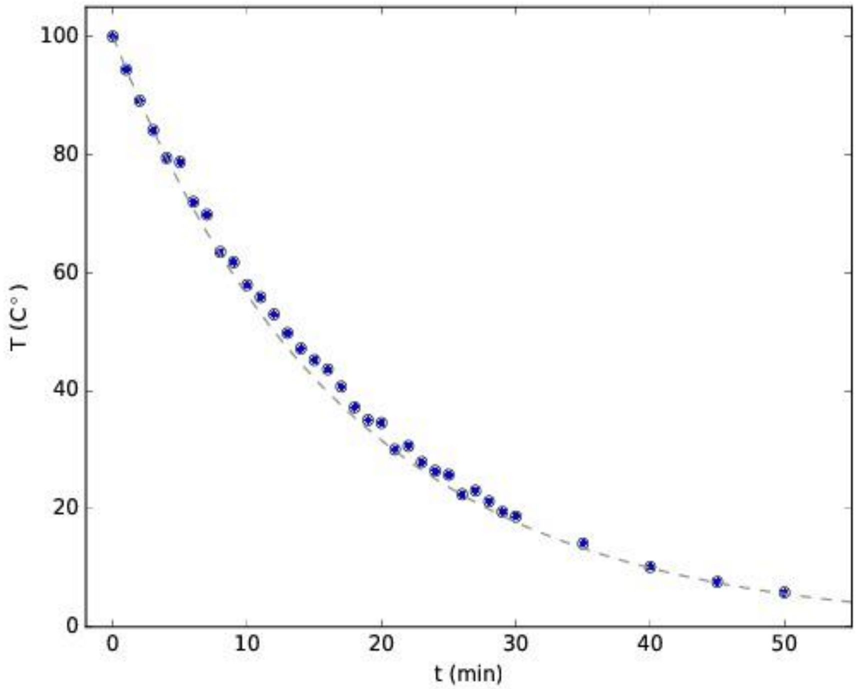

Figure 1