Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.
Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

Chapter I. Entropy.

1. Preparing for Entropy. Remember when we introduced the first law of thermodynamics

$$\Delta U = Q - W$$

and were able to replace W with $p\Delta V$ to obtain

$$\Delta U = Q - p\Delta V .$$

While W is not a state variable, we were able to express it in terms of state variables, namely p and V. The combination $p\Delta V$ is still path dependent and not a state variable. But the components pressure and volume are state variables. We would like to achieve the same goal with the heat transfer term Q. We first isolate the heat transfer using $\Delta U = Q - p\Delta V$.

$$Q = \Delta U + p\Delta V$$

The energy U for an ideal monatomic gas is $U = \frac{3}{2} nR^* T$.

I would like to express this equation in terms of the mass of the gas.

The mass of the gas m and the number of moles n are related through the molar mass M.

$$m = nM$$

Therefore, $n = \frac{m}{M}$ and $U = \frac{3}{2} nR^* T$ leads to

$$U = \frac{3}{2}\frac{m}{M} R^* T .$$

But remember that $R = \frac{R^*}{M}$. The energy then becomes

$$U = \frac{3}{2} mRT$$

From $U = \frac{3}{2} nR^* T$ and $U = \frac{3}{2} mRT$, it is always helpful to remember the following connection.

$$\boxed{nR^* = mR}$$

We have also seen that $c_{V,n} = \frac{1}{n}\frac{dU}{dT} = \frac{3}{2}R^*$.

But I want to use the specific heat at constant volume, meaning per unit mass.

$$U = \frac{3}{2} mRT \quad \Rightarrow \quad c_V = \frac{1}{m}\frac{dU}{dT} = \frac{3}{2}R .$$

Therefore, the energy can be written as $U = mc_V T$.

This form is more desirable because it is more general. The specific heat is not restricted to $c_V = \frac{3}{2}R$. For diatomic and more complicated molecules the molar specific heat is different . Remember our degrees of freedom, where each degree of freedom means $\frac{1}{2}R$. In that case

$$c_V = \frac{1}{m}\frac{dU}{dT} = \frac{f}{2}R$$

The equation $Q = \Delta U + p\Delta V$ with $U = mc_V T$ becomes

$$Q = mc_V \Delta T + p\Delta V .$$

The first term $nc_V \Delta T$ is good. It is path independent. The second term is not good since the change depends on the path. This fact causes Q to be path dependent too and Q is thus not a state variable. Let's use the ideal gas law $pV = nR^* T$ to eliminate the pressure p in $Q = nc_V \Delta T + p\Delta V$. Remember our connection equation $nR^* = mR$. Therefore, the idea gas also is also

$pV = mRT$, which can be expressed as $p = \frac{mRT}{V}$.

Use this equation to eliminate the p in the $p\Delta V$ term in our equation $Q = mc_v \Delta T + p\Delta V$.

$$Q = mc_V \Delta T + p\Delta V \quad \Rightarrow \quad Q = mc_V \Delta T + \frac{mRT}{V}\Delta V$$

We are almost there. The last term can be fixed with a division by T and this division will not mess up the first term.

$$Q = mc_V \Delta T + \frac{mRT}{V}\Delta V \quad \Rightarrow \quad \frac{Q}{T} = mc_V \frac{1}{T}\Delta T + \frac{nR}{V}\Delta V$$

$$\frac{Q}{T} = mc_V \frac{\Delta T}{T} + nR\frac{\Delta V}{V}$$

2. Entropy Definition. Now the complete right side is path independent. We can integrate and the result only depends on the initial and final temperatures and volumes no matter which path we take. We can define the left side as a new variable which we will call ΔS and the associated variable S is a bona fide state variable.

$$\Delta S \equiv \frac{Q}{T} = mc_V \frac{\Delta T}{T} + nR\frac{\Delta V}{V}$$

The infinitesimal form is

$$dS = \frac{\delta Q}{T} = mc_V \frac{dT}{T} + nR\frac{dV}{V}.$$

We can now integrate from the initial state designated as 1 to the final state 2.

$$\int_{S_1}^{S_2} dS = mc_V R\int_{T_1}^{T_2}\frac{dT}{T} + mR\int_{V_1}^{V_2}\frac{dV}{V}$$

$$S\Big|_{S_1}^{S_2} = mc_V R\ln T\Big|_{T_1}^{T_2} + mR\ln V\Big|_{V_1}^{V_2}$$

$$S_2 - S_1 = mc_v R(\ln T_2 - \ln T_1) + mR(\ln V_2 - \ln V_1)$$

$$S_2 - S_1 = mc_V R\ln\frac{T_2}{T_1} + mR\ln\frac{V_2}{V_1}$$

We call S the *entropy*.

If we divide both sides by the mass m of the gas,

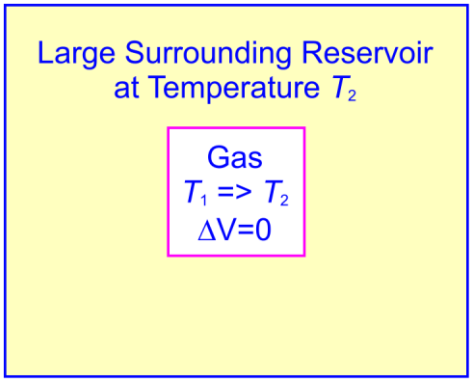
$$dS = \frac{\delta Q}{T} \text{ becomes } ds = \frac{\delta q}{T}.$$

This formula is our equation 17.

$$(17)\ \boxed{ds = \frac{\delta q}{T}}$$

In real life you cannot integrate any of the above parameters because the gas will go through states where there is no uniform temperature and pressure everywhere. Integrations mean that at every infinitesimal step of the way there is a well-defined temperature and pressure everywhere for the gas, which we call such an equilibrium state. To achieve this ideal the gas must change super slowly so temperature and pressure changes uniformly throughout the gas. And at any point, we have an equilibrium state and we can reverse the process an infinitesimal amount. We refer to such an ideal process as *reversible*. In real life, processes cannot be run backwards and are called *irreversible*. Whenever we integrate we are approximating a real life change by a reversible process. Always remember this fact.

3. Entropy Increases or Stays the Same. We have yet to actually state the second law of thermodynamics. It involves the change in entropy for processes. We first consider an ideal gas that receives heat from a large reservoir. This particular example is similar to one found in a text I used when I taught thermodynamics in the 1980s. The text is Francis W. Sears and Gerhard L. Salinger, *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*, 3rd edition (Reading, Massachusetts, Addison-Wesley, 1975).



A gas with fixed volume with initial temperature T_1 is placed in an environment which has a temperature T_2. Such a surrounding environment is called a *heat reservoir*, which means a large surrounding environment that can supply or receive heat with virtually no effect on its temperature because it is so large. Such a heat reservoir is also called a *thermal bath*.

The gas surrounded by the reservoir starts off with temperature T_1 and changes to T_2 due to the thermal bath. There are three cases to consider.

Now, I sneak in the second law of thermodynamics. One way to state this law is

heat flows from hot to cold.

Therefore we have three cases.

a) Case $T_1 < T_2$: heat will flow into the gas bringing its temperature up to T_2.
b) Case $T_1 = T_2$: no heat will be exchanged and the gas will remain at temperature $T_1 = T_2$.
c) Case $T_1 > T_2$: heat will flow out of the gas lowering its temperature to T_2.

Let's consider the first case $T_1 < T_2$. Heat will then flow from the reservoir into the gas. We would like to calculate the change in entropy for the gas and that for the reservoir.

a. Entropy Change for the Gas. We already figured this one out in general. We set $V_1 = V_2$ in

$$S_2 - S_1 = mc_V R \ln\frac{T_2}{T_1} + mR \ln\frac{V_2}{V_1}, \text{ obtaining}$$

$$\Delta S_{\text{gas}} = mc_V R \ln\frac{T_2}{T_1}.$$

The heat flowing into the gas can be expressed through its specific heat at constant volume, which we assume to be constant over the temperature range. This assumption is reasonable and supported in data measurement tables.

$$c_V = \frac{1}{m}\frac{\Delta Q}{\Delta T}\bigg|_V \quad \Rightarrow \quad \Delta Q_{\text{gas}} = mc_V \Delta T = nc_{V,n}(T_2 - T_1)$$

We will need to use this equation when we address what happens to the reservoir next.

b. Entropy change for the Heat Reservoir. The heat reservoir maintains the same temperature T_2 due to its idealized super large volume. It gives up heat $\Delta Q_{\text{gas}} = mc_V \Delta T = mc_V (T_2 - T_1)$ to the gas.

The heat change for the reservoir is therefore negative this heat that the gas receives,

$$\Delta Q_{\text{reservoir}} = -\Delta Q_{\text{gas}} = -mc_V (T_2 - T_1).$$

The reservoir entropy change is easy to determine since it stays at constant temperature T_2.

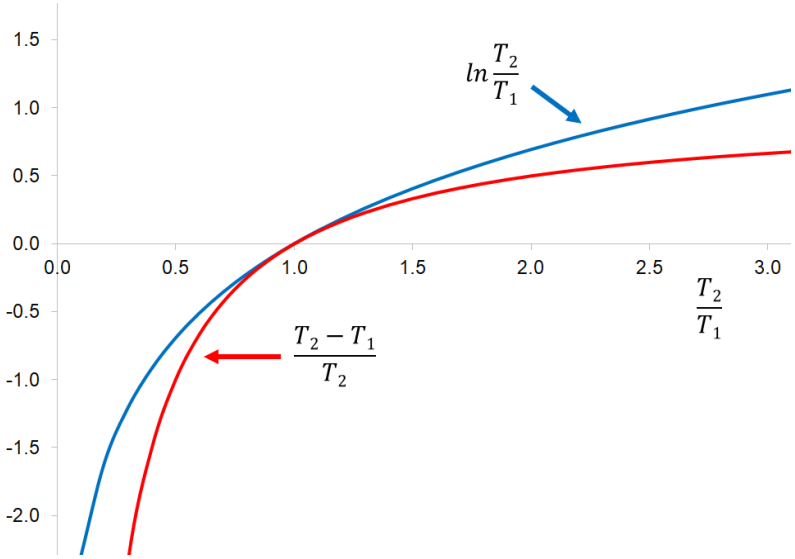
$$\Delta S_{\text{reservoir}} = \frac{\Delta Q_{\text{reservoir}}}{T_2} = -mc_V \frac{(T_2 - T_1)}{T_2}$$

The total change in entropy can be found by adding the two entropy changes.

$$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} = mc_V \ln\frac{T_2}{T_1} - mc_V \frac{(T_2 - T_1)}{T_2}$$

$$\frac{\Delta S_{\text{total}}}{mc_V} = \ln\frac{T_2}{T_1} - \frac{T_2 - T_1}{T_2}$$

We need to compare $\ln\frac{T_2}{T_1}$ with $\frac{T_2-T_1}{T_2}$.



For $T_1 < T_2$ we have $\frac{T_2}{T_1} > 1$ and we find that $\ln\frac{T_2}{T_1} > \frac{T_2-T_1}{T_1}$. Therefore, $\frac{\Delta S_{\text{total}}}{nc_{V,n}} = \ln\frac{T_2}{T_1} - \frac{(T_2-T_1)}{T_1} > 0$.

For $T_2 < T_1$ we have $\frac{T_2}{T_1} < 1$ and we still find $\ln\frac{T_2}{T_1} > \frac{T_2-T_1}{T_1}$. Therefore, $\frac{\Delta S_{\text{total}}}{nc_{V,n}} = \ln\frac{T_2}{T_1} - \frac{(T_2-T_1)}{T_1} > 0$.

The entropy of the universe increases in both cases. The only way to obtain no increase is for $T_2 = T_1$. In that case, the temperature of the gas matches that of the surrounding reservoir and there is no heat exchange. This conclusion demonstrates the amazing richness in our introduction of entropy.

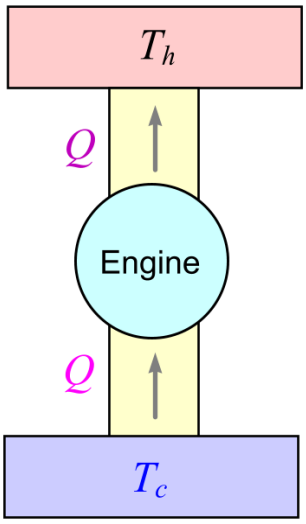
The way to state the second law of thermodynamics is that the entropy of a closed system never decreases. This statement is consistent with our above results. When heat is absorbed, the entropy increases. The system becomes more disordered. Think of gas in a container absorbing heat. The gas particles move even faster in a more chaotic manner. One statement of the second law of thermodynamics is that the disorder in a closed system cannot decrease. Things tend towards disorder.

Second Law of Thermodynamics: The entropy of a closed system cannot decrease.

$$\Delta S \geq 0$$

4. The Second Law of Thermodynamics. For a closed system $\Delta S \geq 0$.

Statement 1. The Clausius Statement of the Second Law of Thermodynamics.



Clausius (1854): *"It is impossible for a self-acting machine working in a cyclic process unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature."*

The entropy change for the left process is

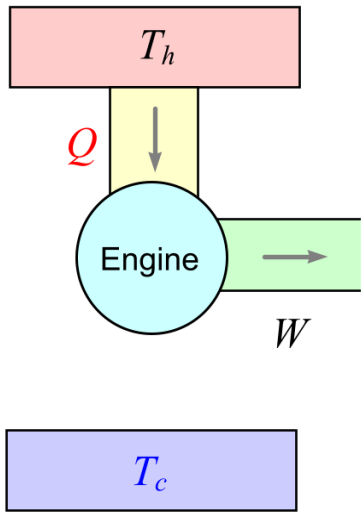
$$\Delta S = \sum \frac{Q}{T} = \frac{(-Q)}{T_c} + \frac{Q}{T_h}.$$

But $T_h > T_c$. Therefore,

$$\Delta S = -\frac{Q}{T_c} + \frac{Q}{T_h} = Q\left(\frac{1}{T_h} - \frac{1}{T_c}\right) = Q\left(\frac{T_c - T_h}{T_h T_c}\right) < 0,$$

which violates the second law of thermodynamics which states $\Delta S \geq 0$ for a closed system. I like to remember this law as "Heat Does Not Flow from Cold to Hot." This quick statement assumes no work is involved and we are talking about the natural flow of things, i.e., spontaneously.

Statement 2. The Kelvin-Planck Statement of the Second Law of Thermodynamics.



Kelvin-Planck: *It is impossible for a device working in a cyclic process to extract heat from a single reservoir and convert it totally to work.*

The change in entropy for this system is

$$\Delta S = \sum \frac{Q}{T} = -\frac{Q}{T_h} < 0,$$

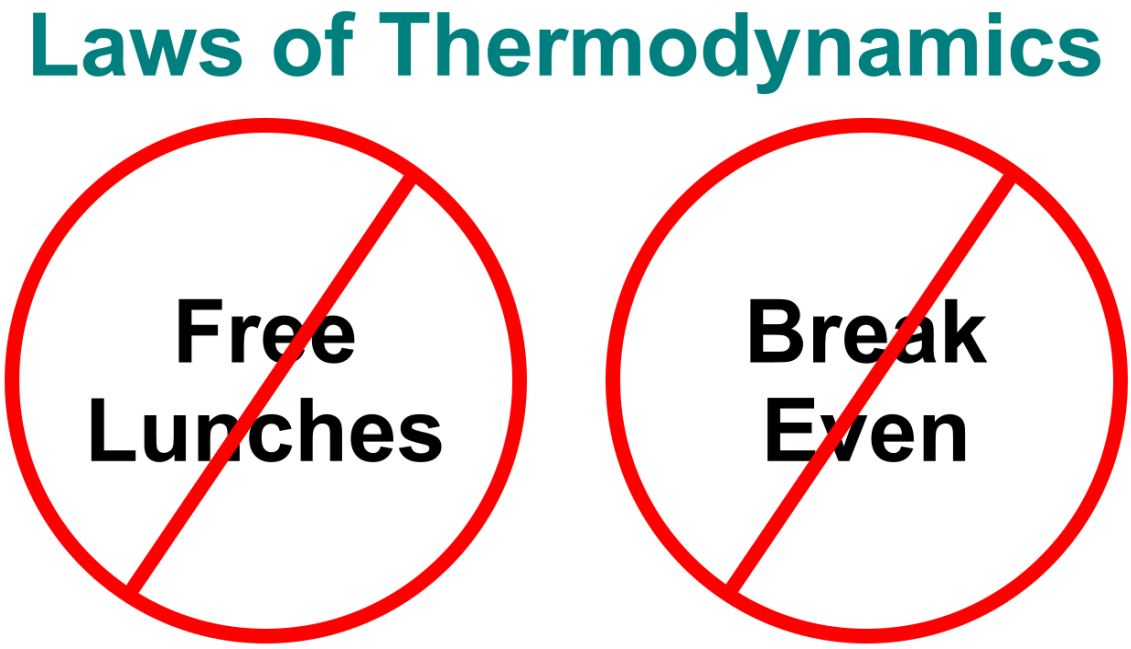
which violates the second law of thermodynamics which states $\Delta S \geq 0$ for a closed system.

The efficiency of the engine shown here is 100%, i.e.,

$$\eta = \frac{W}{Q_{in}} = \frac{Q}{Q} = 1.$$

So you must discard some of your input heat and the efficiency will be less than 100%.

We summarize with signs our two main laws of thermodynamics.



The first law is that there are no free lunches. This law is the law of conservation of energy. The second says you can't break even; you have to waste some of your energy. This law is the law of entropy.

Addendum

In the YouTube video for this chapter I discuss entropy using $x = \frac{T_2}{T_1}$ and the following graph.