Lecture_05

September 28, 2022

1 Entropy

Clausius' theorem states that

$$\oint \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = 0$$

This means that the quantity

$$\int_B^A \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

is a function of state (that is, it has an exact value for a given equilibrium state of the system). Another way of saying this is that this quantity is an exact differential, and is path independant. We are going to now define this function of state as the **entropy** S of the system such that

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

and

$$S(B) - S(A) = \int_B^A \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

Recalling that for an adiabatic process, $\mathrm{d}Q_{\mathrm{rev}} = 0$, this would also mean that there is no change in entropy during this process. As such, an adiabatic process can also be called an isentropic process.

1.1 Irreversibility

S is defined in relation to a reversible change of heat. Taking Clausius' theorem for reversible processes again, we have that

$$\oint \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = 0$$

We are now going to consider a cycle which starts with some irreversible process, followed by a reversible process. Such a process is given in the P-V diagram below.
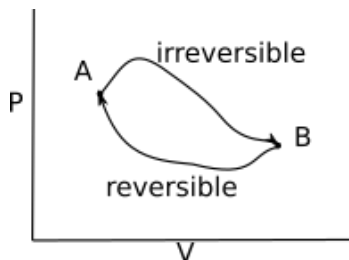
The Clausius' inequality tell us that

$$\oint \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} \leq 0$$

We can then split this integral into two segments

$$\int_A^B \frac{\mathrm{d}Q}{T} + \int_B^A \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} \leq 0$$

which simplifies to

$$\int_A^B \frac{\mathrm{d}Q}{T} \leq \int_A^B \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

This is true no matter how close the curves joining A to B and B to A get. As such, we can also write the change in entropy of a system to be

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} \geq \frac{\mathrm{d}Q}{T}$$

Now consider a thermally isolated system. This means that $\mathrm{d}Q$ is always 0 for this system. Then, for any process within the system, the inequality becomes

$$\mathrm{d}S \geq 0.$$

It's worth considering exactly what this condition is now saying. For any system that is thermally isolated, the entropy will stay the same for reversible processes, or will increase for irreversible processes. This is another way of stating the second law of thermodynamics: **"The entropy of an isolated system tends to a maximum"**.

This has some very fundamental consequences. For example, if the Universe is a isolated system, then it means that entropy of the Universe can only increase.

1.2   Example

Imagine we have a large reservoir at temperature T_R which is placed into thermal contact with a small system at temperature T_S. They both end up at the temperature of the reservoir, T_R. The heat transferred from the reservoir to the system is given by

$$\Delta Q = C(T_S - T_R)$$

where C is the heat capacity of the system. There are two different outcomes here:

1. $T_S > T_R$. This means that heat would be transferred from the system to the reservoir. As such, the entropy of the system would decrease as it gets colder and the entropy of the reservoir would increase as it warms up.
2. $T_S < T_R$. This means that heat would be transferred from the reservoir to the system. As such, the entropy of the reservoir would decrease as it gets colder and the entropy of the system would increase as it warms up.

Let's explicitly calculate the entropy change of both the system and reservoir:

$$\Delta S_{\text{reservoir}} = \int \frac{\mathrm{d}Q}{T} \tag{1}$$

$$= \frac{1}{T_R} \int \mathrm{d}Q \tag{2}$$

$$= \frac{\Delta Q}{T_R} \tag{3}$$

$$= \frac{C(T_S - T_R)}{T_R} \tag{4}$$

$$\tag{5}$$

The entropy of the system is given by

$$\Delta S_{\text{system}} = \int \frac{\mathrm{d}Q}{T} \tag{6}$$

$$= \int_{T_S}^{T_R} \frac{C\mathrm{d}T}{T} \tag{7}$$

$$= C \ln \frac{T_R}{T_S} \tag{8}$$

So the entropy of the system is allowed to increase or decrease, as is that of the reservoir. But the entropy of the Universe, which is given by

$$\Delta S_{\text{Universe}} = \Delta S_{\text{reservoir}} + \Delta S_{\text{system}} \tag{9}$$

$$= \frac{C(T_S - T_R)}{T_R} + C \ln \frac{T_R}{T_S} \tag{10}$$

$$= C \left[\frac{T_S}{T_R} + \ln \frac{T_R}{T_S} - 1 \right] \tag{11}$$

The below figure plots this expression and shows that even though the entropy of the system and reservoir may increase or decrease individually, their combined change is always positive!
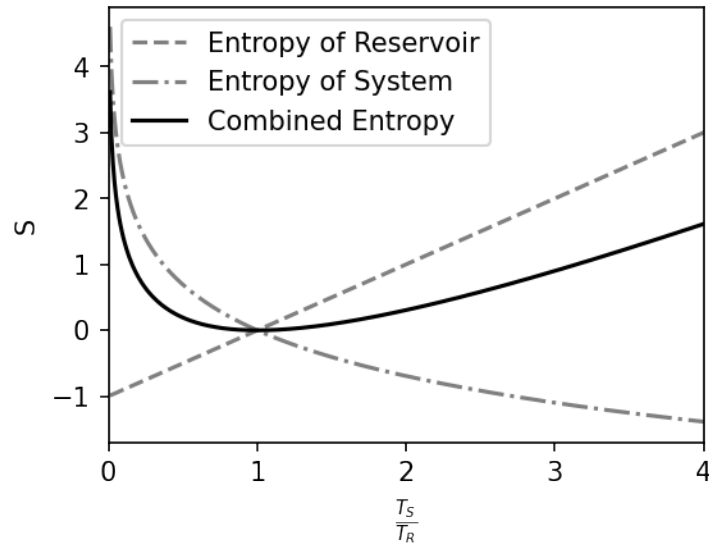
1.3 Revisiting the first law

Ok, armed with this definition of entropy, let's consider again the first law of thermodynamics, which states that

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$$

For a reversible change, we now have that

$$\mathrm{d}Q = T\mathrm{d}S$$

by rearranging Clausius' law. We also know that

$$\mathrm{d}W = -P\mathrm{d}V$$

This means that

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

We have derived this assuming everything is reversible. However, all of the quantities in the previous equation are functions of state - that is, they are path independant. This means that this equation also holds for irreversible changes. This might not seem immediately obvious. As a quick check, remember that for irreversible changes we have that

$$\mathrm{d}Q \leq T\mathrm{d}S$$

while

$$\mathrm{d}W \geq -P\mathrm{d}V.$$

So for irreversible changes, $\mathrm{d}Q$ decreases while $\mathrm{d}W$ increases, meaning $\mathrm{d}U$ is balanced. As such

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

is true **for any process**! Now, using one of the tricks we used earlier, given that U is now only a function of S and V, we can write U as

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

let's us identify pressure and temperature as

$$T = \left(\frac{\partial U}{\partial S}\right)_V \tag{12}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{13}$$

$$\tag{14}$$

1.4 Summary

Thus, the important equations for us are

1. $\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$, which is always true.
2. $\mathrm{d}Q = T\mathrm{d}S$, which is true for reversible changes.
3. $\mathrm{d}W = -P\mathrm{d}V$, which is true for reversible changes.
4. $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$, which is always true.

For irreversible changes, $\mathrm{d}Q \leq T\mathrm{d}S$ and $\mathrm{d}W \geq -P\mathrm{d}V$.

2 The Joule Expansion

Consider the following isolated system. Imagine we have a 2 containers, each of volume V_0, and which are initially isolated from each other by a valve. In the left container, we have an ideal gas with initial pressure P_i, and in the right, we have a vacuum. The ideal gas is described by the equation of state $P_i V_0 = N k_B T_i$.
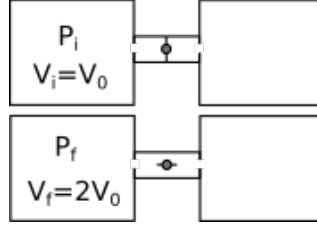
We then open the valve, and the gas rapidly expands to fill both containers. At this stage, the gas will fill a volume of $2V_0$ and have a temperature and pressure of T_f and P_f respectively. It's equation of state is thus $P_f 2 V_0 = N k_B T_f$.

Since the entire system is thermally isolated, we have that $\Delta U = 0$. Recalling from earlier that the internal energy, U, of an ideal gas only depends on temperature, this then means that $\Delta T = 0$, and so $T_i = T_f$. As such, we get

$$P_i V_0 = N k_B T_i = P_f 2 V_0 \tag{15}$$

$$P_f = \frac{P_i}{2} \tag{16}$$

However, calculating the entropy associated with this change is difficult. Immediately after opening the valve, the gas will expand rapidly, meaning it is not in equilibrium and will not be undergoing a reversible process. However, entropy is a function of state. This means that the difference in entropy between the gas prior to the valve opening and after opening the valve and letting the gas reach equilibrium after expanding irreversibly **is the same** as if we had reverisble expanded the gas, as the change in entropy is path independant.

As such, we can pretend that the gas were expanded, say, isothermally, calculate the change in the entropy for this expansion, and it will be the same as for the irreversible process. this gives

$$\Delta S = \int_i^f \mathrm{d}S \tag{17}$$

$$= \int_{V_i}^{V_f} \frac{P}{T} \mathrm{d}V \tag{18}$$

$$= \frac{1}{T} \int_{V_0}^{2V_0} P \mathrm{d}V \tag{19}$$

$$= \frac{1}{T} \int_{V_0}^{2V_0} \frac{N k_B T}{V} \mathrm{d}V \tag{20}$$

$$= N k_B \int_{V_0}^{2V_0} \frac{1}{V} \mathrm{d}V \tag{21}$$

$$= N k_B \ln 2 \tag{22}$$

$$\tag{23}$$