

Muddiest Point – Entropy and Reversible

I am confused about entropy and how it is different in a reversible versus irreversible case.

Note: Some of the discussion below follows from the previous muddiest points comment on the general idea of a reversible and an irreversible process. You may wish to have a look at that comment before reading this one.

Let's talk about entropy first, and then we will consider how "reversible" gets involved. Generally we divide the universe into two parts, a system (what we are studying) and the surrounding (everything else). In the end the total change in the entropy will be the sum of the change in both,

$$dS_{\text{total}} = dS_{\text{system}} + dS_{\text{surrounding}}.$$

This *total* change of entropy has only two possibilities: Either there is no spontaneous change (equilibrium) and $dS_{\text{total}} = 0$, or there is a spontaneous change because we are not at equilibrium, and $dS_{\text{total}} > 0$. Of course the entropy change of each piece, system or surroundings, can be positive or negative. However, the second law says the sum must be zero or positive. Let's start by thinking about the entropy change in the system and then we will add the entropy change in the surroundings.

Entropy change in the system: When you consider the change in entropy for a process you should first consider whether or not you are looking at an isolated system. Start with an isolated system. An isolated system is not able to exchange energy with anything else (the surroundings) via heat or work. Think of surrounding the system with a perfect, rigid insulating blanket. If the system is isolated, then you have two choices: (1) You are at equilibrium and there will be no change in the entropy, ie no spontaneous processes. (2) You are not at equilibrium and the entropy will increase as the system spontaneously heads for equilibrium. For example, think of having one side of your system hotter than the other side, and spontaneously the two sides equilibrate to the same temperature. Your book refers to this as the "produced entropy" or dS_{prod} , and you should associate this with the spontaneous drive to equilibrium. Note that since the system is isolated, there is no exchange of energy with the surrounding via heat, and therefore $q = 0$. The entropy change in the *isolated* system is only the result of spontaneous change toward equilibrium.

Add the surroundings: Now allow the system to interact with the surroundings. This means energy can be exchanged via heat and work. In this case we still have any increase in entropy due to our system being away from equilibrium and spontaneously changing, the "produced" entropy or dS_{prod} . However now we also have any change in the entropy of the system due to the exchange of energy between the system and the surroundings via heat, which the book refers to as the entropy change from exchange dS_{exch} . Now the total *for the system* is

$$dS_{\text{system}} = dS_{\text{prod}} + dS_{\text{exch}}.$$

In an isolated system $dS_{\text{exch}} = 0$.

Consider the isothermal expansion of an ideal gas. The gas is the system, and the rest is the surroundings. If the gas expands, then it is doing work on the surroundings. The conversion of energy in the gas to work would cause the temperature to drop (remember the adiabatic expansion). However, since we declared this to be an isothermal expansion energy must flow via heat into the gas from the surroundings to maintain the temperature. So, by definition an isothermal expansion is not isolated. Note that the amount of energy that flows into the gas via heat to maintain the temperature is exactly the amount needed to replace the energy used by the gas for the work in the expansion.

Now we have both the contribution to the entropy change from the system and from the surroundings. Realize that the change in the surroundings due to exchange of energy via heat is exactly equal and opposite to the change in the system due to the exchange of energy via heat, $\delta q_{\text{system}} = -\delta q_{\text{surrounding}}$ (it is the same heat). The entropy due to exchange is the heat over the temperature, $dS_{\text{exch}} = \frac{\delta q}{T}$. If we put the whole picture together we have,

$$\begin{aligned} dS_{\text{total}} &= dS_{\text{system}} + dS_{\text{surrounding}} \\ &= \underbrace{(dS_{\text{prod}} + dS_{\text{exch}})}_{dS_{\text{system}}} + dS_{\text{surrounding}} \\ &= \underbrace{\left(dS_{\text{prod}} + \frac{\delta q_{\text{system}}}{T}\right)}_{dS_{\text{system}}} + \underbrace{\frac{\delta q_{\text{surrounding}}}{T}}_{dS_{\text{surrounding}}} \end{aligned}$$

And using $\delta q_{\text{system}} = -\delta q_{\text{surrounding}}$,

$$dS_{\text{total}} = \underbrace{\left(dS_{\text{prod}} + \frac{\delta q_{\text{system}}}{T}\right)}_{dS_{\text{system}}} - \underbrace{\frac{\delta q_{\text{system}}}{T}}_{dS_{\text{surrounding}}} \quad (1)$$

Note that the entropy change due to exchange of energy via heat is equal and opposite for the system and surroundings. If the system is at equilibrium then there is no spontaneous change and we know that the total change in the entropy should be zero (although the change in the system and surroundings may not be zero, they will be equal in amplitude with opposite sign). At equilibrium $dS_{\text{prod}} = 0$ and the last two terms cancel to give a total change of zero for the entropy, $dS_{\text{total}} = 0$ at equilibrium. If the system is not at equilibrium, then we will have $dS_{\text{prod}} > 0$ and $dS_{\text{total}} > 0$ indicating spontaneous change.

Reversible vs. Irreversible. Now consider how we calculate the entropy change. Start with the entropy change for the system,

$$dS_{\text{system}} = dS_{\text{prod}} + \frac{\delta q_{\text{system}}}{T}. \quad (2)$$

It is not always obvious how you might calculate dS_{system} , but since entropy is a state function we can choose any path we like to calculate the change and it must be the same for all paths

that start and end in the same places. We choose the reversible path since it is well defined and we know how to calculate it. For a reversible process the system is at equilibrium at every point along the path (see previous Muddiest points comment on reversible). This means that for a reversible path $dS_{\text{prod}} = 0$ in equation 2

$$dS_{\text{system}} = \frac{\delta q_{\text{system,rev}}}{T}. \quad (3)$$

Calculate the reversible path: Let's use our standard model system, the isothermal expansion of an ideal gas, as an example (figure 1).

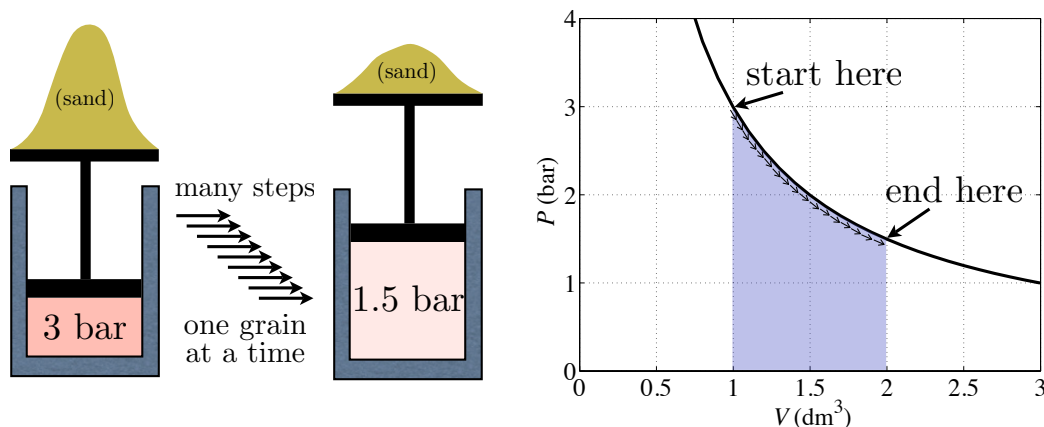


Figure 1: Consider a reversible isothermal expansion where you remove one grain of sand at a time. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

Since this is isothermal we know that it does interact with the surroundings and there will be the flow of energy via heat. We can calculate the heat using the first law, $dU = \delta q + \delta w$, and the fact that we know for an ideal gas that the energy, U , only depends on the temperature. This means that $dU = 0$ for our isothermal process,

$$dU = 0 \text{ (isothermal, ideal)} \quad \longrightarrow \quad \delta q = -\delta w$$

We know how to calculate work, $\delta w = -PdV$, and we know how the pressure changes with volume during the *reversible* process since it is at equilibrium at all times, $P = \frac{RT}{V}$.

$$\delta q_{\text{rev}} = -\delta w_{\text{rev}} = \frac{RT}{V} d\bar{V}$$

Using equation 3,

$$dS_{\text{system}} = \frac{\delta q_{\text{system,rev}}}{T} = \frac{R}{V} d\bar{V}$$

Integrating over the process we get ΔS_{system} , and this is just integrating over the work divided by the temperature.

$$\Delta S_{\text{system}} = \int_{\bar{V}_{\text{start}}}^{\bar{V}_{\text{finish}}} \frac{R}{V} d\bar{V} = R \ln \left(\frac{\bar{V}_{\text{finish}}}{\bar{V}_{\text{start}}} \right)$$

For the expansion this is a positive number, just as we expected. Allowing the same amount of gas at the same temperature to exist in a larger volume increases the disorder (think of placing the same number of items in a smaller space as being more organized). From the molecules perspective this actually moved the translational energy levels closer together, making more of them accessible at the given temperature. More equally probably states to choose from means more disorder.

Note that while we used a reversible path to calculate the entropy change of the system, S is a state function, so this is the entropy change of the system for any isothermal path, reversible or not.

We also now know the entropy change for the surroundings. It is generally true from equation 1,

$$dS_{\text{surroundings}} = \frac{\delta q_{\text{surroundings}}}{T} = -\frac{\delta q_{\text{system}}}{T} \quad (4)$$

And for the *reversible process* we have $dS_{\text{prod}} = 0$ giving us in equation 1,

$$dS_{\text{surroundings}} = -dS_{\text{system}} \quad (\text{reversible})$$

Integrating then gives us,

$$\Delta S_{\text{surroundings}} = -\Delta S_{\text{system}} = -R \ln \left(\frac{\bar{V}_{\text{finish}}}{\bar{V}_{\text{start}}} \right) \quad (\text{reversible}) \quad (5)$$

As we expected, for the reversible path (ie at equilibrium at all times) the change in the entropy of the surroundings is equal amplitude and opposite sign of the change in the entropy of the system. This is not the case for an irreversible process.

Now consider an irreversible path: Let's use our standard irreversible isothermal expansion where we expand at constant pressure, figure 2.

Now we start with *the fact that the entropy is a state function, and therefore the entropy change for our system must be the same as it was in the reversible case.*

$$\Delta S_{\text{system}} = R \ln \left(\frac{\bar{V}_{\text{finish}}}{\bar{V}_{\text{start}}} \right)$$

However, this time we know that some of the entropy change in the system was from spontaneous change since this was not a reversible process. Therefore $dS_{\text{prod}} > 0$. Looking at equation 2, we can see that this also means that,

$$dS_{\text{system}} - dS_{\text{prod}} = \frac{\delta q_{\text{system}}}{T}$$

$$\frac{\delta q_{\text{system}}}{T} < dS_{\text{system}} \quad (6)$$

Since the change in the entropy of the system is the same as the reversible process, and the total change in entropy ($dS_{\text{total}} = dS_{\text{system}} + dS_{\text{surrounding}}$) is now positive since we have

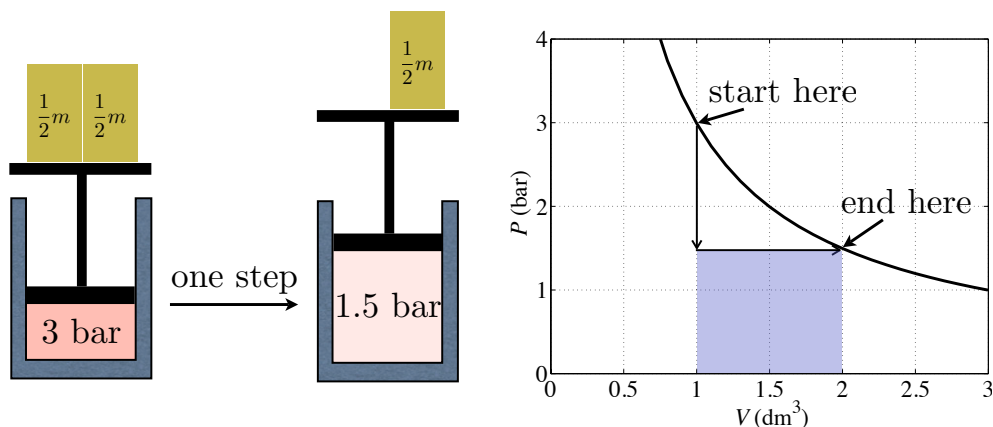


Figure 2: Consider an irreversible isothermal expansion where you lower the external pressure all at once by knocking off half the mass. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

spontaneous change, then there must be less change in the entropy of the surroundings. This can be seen in equations 6 and 4.

We still use equation 4 to calculate the change in the entropy of the surroundings. However, this time the constant pressure process has less work done by the gas than the reversible process (compare the area under the process in figures 1 and 2). This means less energy is transferred as heat to maintain a constant temperature (remember $\delta q = -\delta w$ in this case). Therefore the change in the entropy of the surroundings is less than the reversible case. Using equation 4, we need the heat for the constant pressure process to calculate $\Delta S_{\text{surroundings}}$.

$$dS_{\text{surroundings}} = \frac{\delta q_{\text{surroundings}}}{T} = -\frac{\delta q_{\text{system}}}{T}$$

We still get this from the first law, the fact that $dU = 0$, and the definition of the work. This time using the work for the constant pressure process ($\delta w = Pd\bar{V}$).

For the system we have,

$$dU = \delta q + \delta w \xrightarrow{dU=0} \delta q_{\text{system}} = -\delta w_{\text{system}} \xrightarrow{\delta w_{\text{system}} = -Pd\bar{V}} \delta q_{\text{system}} = Pd\bar{V}$$

And for the surroundings,

$$dS_{\text{surroundings}} = -\frac{\delta q_{\text{system}}}{T} = -\frac{P}{T}d\bar{V}$$

Integrate with constant P and T on both sides,

$$\Delta S_{\text{surroundings}} = -\int_{\bar{V}_{\text{start}}}^{\bar{V}_{\text{finish}}} dV = -\frac{P\Delta\bar{V}}{T} \quad (\text{constant } P, \text{ irreversible}) \quad (7)$$

Compare this result with the change in the entropy of the surroundings for the reversible process, equation 5. Note that once again we expected energy as heat to flow from the surroundings to the system to maintain constant temperature for an expansion. The loss of energy as heat from the surroundings should cause a reduction in the entropy of the surroundings, and we get a negative number as expected. Of course the total entropy change is still positive thanks to the larger increase in the system.

Although we did not plug in any actual numbers, you can see that the reversible and irreversible paths have different changes in the entropy of the surroundings. Remember that they have the same change in entropy for the system. For the expansion, we know that less work was done by the gas in the irreversible constant pressure case compared to the reversible case (see figures 1 and 2). Less work means less heat was needed to maintain a constant temperature, which means a smaller change in the entropy of the surroundings.

Finally note that the entropy change in the system is the same for both paths. It is the entropy change in the surroundings that is different when comparing a reversible (think equilibrium, no spontaneous) to an irreversible (not at equilibrium, spontaneous change toward equilibrium) process. And, while the entropy change in the system remains the same for the different paths, what changes is how it is divided between produced (from spontaneous change) and exchanged (from energy transferred via heat).

Suggested Activities

- Using the actual values in the figure captions, calculate the actual change in entropy, for the system, the surroundings, and the total for both the reversible and the irreversible (constant P) paths. See how they compare and if you get what you expect.
- Do the same calculations, but this time for the compression. What do you expect for the sign of the entropy change of the system? Which way will energy flow as heat? What should the sign of the entropy change of the surroundings be? What should the total entropy change be for each case? Compare your results to the expansion. The corresponding figures for the compression are shown on the next page.

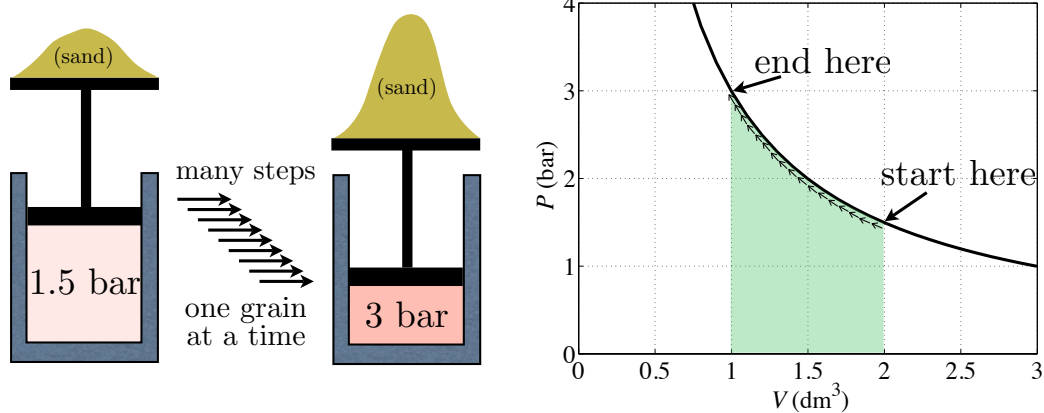


Figure 3: Consider a reversible isothermal compression where you add one grain of sand at a time. The plot on the right is for 0.12 moles of an ideal gas at 300 K.

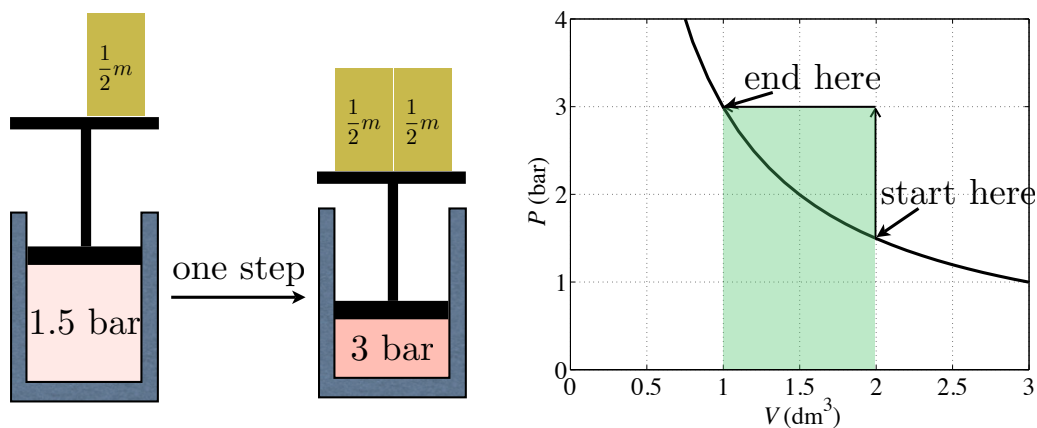


Figure 4: Consider an irreversible isothermal compression where you raise the external pressure all at once by putting the mass back. The plot on the right is for 0.12 moles of an ideal gas at 300 K.