

Lecture 13

An example incorporating change in entropy

Consider a large reservoir at temperature T_R is placed in thermal contact with a small system T_s . They both ultimately end up at the ~~reservoir~~ T_R . The heat transfer from the reservoir to the system is,

$$\Delta Q = C(T_R - T_s), \text{ where } C \text{ is the heat capacity of the system.}$$

(i) If $T_R > T_s$, heat is transferred from the reservoir to the system. The system warms up, and its entropy increases. The entropy of the reservoir decreases since heat flows out of it.

(ii) If $\cancel{T_R} < T_s$, the vice-versa happens.

Now, the entropy change in the reservoir, which is at a constant temperature is given by,

$$\Delta S_{\text{res}} = \int \frac{dQ}{T_R} = \frac{1}{T_R} \int dQ = \frac{1}{T_R} C(T_s - \cancel{T_R})$$

The change in entropy of the system is given by,

$$\Delta S_{\text{sys}} = \int \frac{dQ}{T} = \int_{T_s}^{T_R} \frac{CdT}{T} = C \ln \frac{T_R}{T_s}$$

So, the total change in entropy of the universe is,

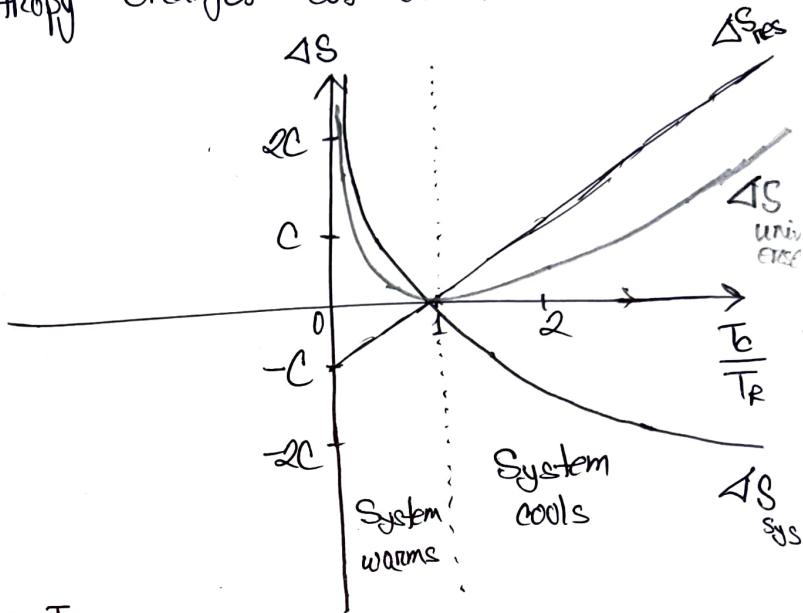
$$\Delta S_{\text{universe}} = \Delta S_{\text{res}} + \Delta S_{\text{sys}} = C \left[\frac{T_s}{T_R} - 1 + \ln \frac{T_R}{T_s} \right]$$

We plot these entropy changes as a function of $\frac{T_s}{T_R}$.

$$\Delta S_{\text{res}} = C \frac{T_s}{T_R} - C$$

$$\begin{aligned} \Delta S_{\text{sys}} &= C \ln \frac{T_R}{T_s} \\ &= -C \ln \frac{T_s}{T_R} \end{aligned}$$

$$\Delta S_{\text{universe}} = C \frac{T_s}{T_R} - C + \ln \frac{T_R}{T_s}$$

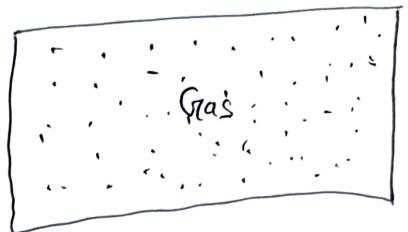
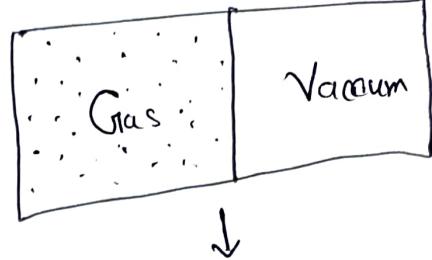


The plot clearly shows that, $\Delta S_{\text{universe}} > 0$ where ΔS_{res} and ΔS_{sys} can be both positive and negative. Equality holds if both of them are at the same temperature.

The Joule expansion

We consider our good old Joule expansion of ideal gas again. We have one mole of ideal gas (at pressure P_i and temperature T_i) which is confined

to the left side of ~~the~~ a thermally isolated container and occupies a volume of V_0 . The right side of the container is vacuum. The divider between the two containers is suddenly opened and the gas now occupies the entire volume $2V_0$ (and now with temperature T_f and pressure P_f). Both containers are thermally isolated from their surroundings. For the initial state, ideal gas law implies,



$$P_i V_0 = RT_i$$

and for the final state, ~~$P_f \times 2V_0 = RT_f$~~

We already discussed that for Joule expansion of ~~ideal~~ ideal gas $\Delta U = 0$ and $\Delta T = 0$, and so $T_f = T_i$.

$$\therefore \frac{P_i V_0}{R} = \frac{2 P_f V_0}{R}$$

$$\therefore P_f = \frac{P_i}{2}$$

Now, what is the change in entropy? Clearly there is no heat involved, and you might assume that there might be no change in entropy. However, the process is sudden, and you can't use $dS = \frac{dQ_{rev}}{T}$

for calculating the change in entropy. The process is not reversible. However, the system starts from an equilibrium state and after the expansion it will reach another equilibrium state. So, entropy is defined in these states, and we can calculate this using $dU = TdS - pdV$.

If we had gone through a quasi-static slow isothermal expansion by inputting heat into the system and that will push the barrier to the end of the box. The final state is same as Joule expansion, and we can use this to calculate the change in entropy.

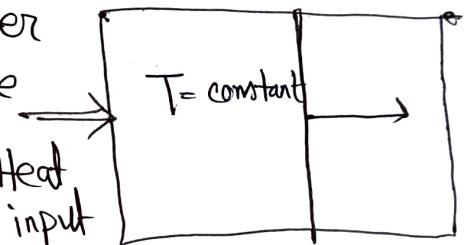
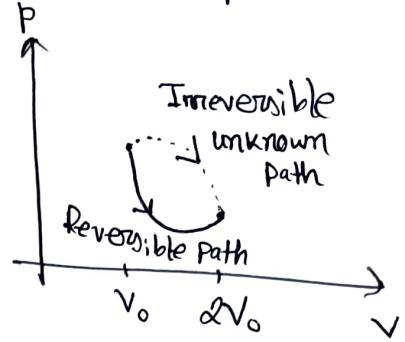
$$\text{Now, } dU = TdS - pdV$$

For the reversible isothermal process, $dU = 0$

$$\therefore TdS = pdV$$

$$\text{Now, } \Delta S = \int_i^f dS = \int_{V_0}^{2V_0} \frac{pdV}{T} = \int_{V_0}^{2V_0} \frac{RdV}{V} = R \ln V \Big|_{V_0}^{2V_0} = R \ln 2$$

This is the increase of entropy of the system in Joule expansion also, since entropy is a state function, and initial and final states are same.



However for an isothermal process, the system is not isolated (since heat flow is permitted). Then, we know, for an isolated reversible process,

$$\Delta S_{\text{universe}} = 0$$

$$\Rightarrow \Delta S_{\text{gas}} + \Delta S_{\text{surrounding}} = 0$$

$$\therefore \Delta S_{\text{surrounding}} = -R \ln 2$$

For Joule expansion, however, the system is thermally isolated. So, the entropy of the surrounding does not change. And it's an irreversible process. So entropy will increase.

$$\therefore \Delta S_{\text{gas}} = R \ln 2 \quad \Delta S_{\text{surrounding}} = 0$$

$$\therefore \Delta S_{\text{universe}} = R \ln 2$$

Now, in Joule expansion, $\Delta Q = 0$, $\Delta V = 0$. But should that mean $\Delta S = \frac{\Delta Q}{T} = 0$? The answer is simply no.

This is because, $dQ = TdS$ is only true for reversible changes. For irreversible changes, $dQ < TdS$.

Since T is constant, $\Delta Q < T\Delta S$. Here, $\Delta Q = 0$ and $\Delta S = R \ln 2$ and we see that, indeed, $\Delta Q < T\Delta S$ in the irreversible Joule expansion.

The entropy of mixing

Consider two different ideal gases (1 and 2) which are in two vessels with volume xV and $(1-x)V$ separated by a barrier. Both the gases are at same pressure p and temperature T .

$$\text{Now, } PV = Nk_B T \Rightarrow \frac{P}{k_B T} = \frac{N}{V}$$

Since P and T are same,

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} \Rightarrow \frac{N_1}{xV} = \frac{N_2}{(1-x)V}$$

$$\therefore \frac{N_1}{N_2} = \frac{x}{1-x}$$

If total number of molecules is N , then, $N_1 = xN$ and $N_2 = (1-x)N$.

Now, if the barrier is opened, the gases will spontaneously mix and the entropy will increase. Like quasi-static

Joule expansion, we consider isothermal expansion of gas 1 from xV to V volume and of gas 2

from $(1-x)V$ to V volume.

$$\therefore \Delta S = \int_i^f \frac{dQ}{T} = \int \frac{T dS}{T} = \int \frac{PV}{T}$$

$$\therefore \Delta S = x \underbrace{Nk_B}_{xV} \frac{dV_1}{V_1} + (1-x) \underbrace{Nk_B}_{(1-x)V} \frac{dV_2}{V_2}$$

| $PV = Nk_B T$

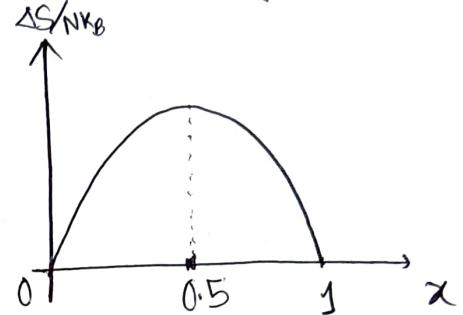
$$= x Nk_B \ln \frac{V}{xV} + (1-x) Nk_B \ln \frac{V}{(1-x)V}$$

$\therefore \Delta S = - Nk_B [x \ln x + (1-x) \ln (1-x)]$

—①

The equation is plotted in the figure.

Clearly for $x=0$ and $x=1$ there is no change in entropy, which should perfectly make sense.



The maximum change in entropy is for $x=0.5$, which is $\Delta S = Nk_B \ln 2$. This expression for $x=0.5$ has also a simple statistical interpretation. Before, gas at 1 was on left hand side. So, the accessible microstate was confined to the left portion only. When it occupies the whole region, for each accessible microstate in the left side, now we have another accessible microstates on the right side. Therefore, if there was previously 1 particle with say, 10 ~~partic~~ microstates, it will be 10×2 now. If there were 2 particles with 50 ~~partic~~ microstates, there will be 50×2×2 microstates. In general, if there were Ω microstates previously, now, we will have $\Omega \times 2^N$ microstates for N .

number of particles.

$$\therefore S' = k_B \ln \Omega \times 2^N = k_B \ln \Omega + k_B \ln 2^N$$

$$\Rightarrow S' = S + N k_B \ln 2$$

$$\therefore \Delta S = N k_B \ln 2$$

which matches with our thermodynamic calculations.

We have assumed here that gas 1 and gas 2 are distinguishable. Like, if it was oxygen and nitrogen, one could measure the mass (or any other property) to distinguish them. But, what if they were indistinguishable? The mixing would then change nothing and so the entropy change should be zero. This is because the process is ~~irreversible~~. You can just put the barrier at place, and everything is like before. But, one can argue, from a different perspective. One could say, both the gases have undergone Joule expansion, and so, the total change in entropy must be $\Delta S = N k_B \ln 2$. Hmm, paradox?

Yes, this paradox is known as Gibbs paradox, which was solved by Gibbs himself. I want you to dive in the solution to the paradox.

Say, there are ~~w~~ number of macrostates possible. There are Ω_i microstates in the i th macrostate and total number of microstates is $\sum_i \Omega_i = \Omega$. The probability that the system is in i th macrostate is given by, $P_i = \frac{\Omega_i}{\Omega}$.

Now, total entropy, $S_{\text{tot}} = K_B \ln \Omega$

$$= K_B \sum_i \frac{\Omega_i}{\Omega} \ln \Omega \quad \text{since } \sum_i \frac{\Omega_i}{\Omega} \ln \Omega = \frac{\ln \Omega}{\Omega} \sum_i \Omega_i = \frac{\ln \Omega}{\Omega} \Omega = \ln \Omega$$

$$= K_B \sum_i P_i \ln \Omega = K_B \sum_i P_i \left[\ln \frac{\Omega}{\Omega_i} + \ln \Omega_i \right]$$

$$\therefore S_{\text{tot}} = -K_B \sum_i P_i \ln P_i + K_B \sum_i P_i \ln \Omega_i$$

Now, the second term corresponds to the average entropy of microstates,

$$\langle S_{\text{micro}} \rangle = \langle S_i \rangle = \sum_i P_i S_i = \sum_i P_i K_B \ln \Omega_i = K_B \sum_i P_i \ln \Omega_i$$

When the system is in equilibrium, it settles to one macrostate with $P_i^* \approx 1$ in thermodynamic limit. Then,

$$S_{\text{tot}} \approx 0 + K_B \ln \Omega_i^*$$

$$\therefore S_{\text{tot}} = K_B \ln \Omega_i^*$$

which is the general form of entropy that we

~~At, in equilibrium, $\Rightarrow P_i = \frac{1}{\Omega}$ and $\Omega_i = \Omega P_i =$~~

Gibbs expression of entropy is, $S_{\text{Gib}} = -K_B \sum_i P_i \ln P_i$

Maxwell's demon

Blundell 14.7 — Page 149

Gibbs entropy: Entropy and probability

Entropy is well defined in a microcanonical ensemble, and it is given by the Boltzmann formula, $S_B = k_B \ln \Omega$, where Ω is the number of microstates corresponding to the equilibrium macrostates. However, in canonical ensemble, the system exchanges energy with the reservoir, so the system is not in a fixed macrostate of fixed energy, rather in different macrostates.

Consider that we don't just have the system, S , but we have a large number of identical copies of S , in total the number is W . Each system lives in a particular microstate i with energy E_i . If the probability of the microstate occurring during fluctuation is P_i , and if W is very large, then the number of systems that is in i^{th} microstate is simply $n_i = P_i W$. To find the entropy, we can treat the whole collection of systems be in microcanonical ensemble of total fixed energy,

$$\sum_i P_i E_i = E$$

$$\text{with } \sum_i P_i = 1$$

$$\sum n_i = W$$

$$\text{since } \sum n_i = \sum P_i W$$

$$= W \sum P_i = W$$

which is total number of systems

If there are total m such microstates, then, then, we only have to figure out how many ways we can put A_1, A_2, \dots, A_m system into W system into m groups of sizes n_1, n_2, \dots, n_m . This is simply a combinatorics problem, and the number is given by,

$$\Omega = \frac{W!}{n_1! n_2! \dots n_m!}$$

$$\ln \Omega = \ln W! - \ln n_1! - \ln n_2! - \dots - \ln n_m!$$

$$= W \ln W - W - n_1 \ln n_1 + n_1 - n_2 \ln n_2 + n_2 - \dots$$

$$= W \ln W - n_1 \ln n_1 - n_2 \ln n_2 - \dots - n_m \ln n_m + (\sum n_i - W)$$

$$= W \ln W - \sum n_i \ln n_i = W \ln W - W \sum \frac{n_i}{W} \ln \frac{W}{n_i}$$

$$= W \ln W - W \sum \frac{n_i}{W} \ln W - W \sum p_i \ln p_i$$

$$= W \ln W - \ln W \sum n_i - W \sum p_i \ln p_i$$

$$= -W \sum p_i \ln p_i$$

$$\therefore S_e = -k_B W \sum p_i \ln p_i$$

But, this is for the whole ensemble, and entropy is additive. So, the entropy of the system is,

$$S = \frac{S_e}{W} \quad \boxed{\therefore S = -k_B \sum p_i \ln p_i}$$

This is the form of Gibbs' entropy. This was rediscovered by Shannon few decades later, known as Shannon entropy for classical information system or Von-Neumann

entropy in quantum systems.