

B: Time's Arrow

Let's look at how entropy changes in some simple and familiar systems.

Simple systems

In order to focus on entropy, it helps to consider isolated systems in which all the other extensive variables are fixed by virtue of rigid, impermeable and insulating walls. To then interrogate spontaneous processes in the simplest way, we divide the isolated system into just two subsystems, A and B, each initially at internal equilibrium and consider what happens when the boundary between them is changed to allow transfers.

The convenience of an isolated system is that we know that extensive quantities can only be redistributed between the subsystems:

$$dE = dE_A + dE_B = 0 \quad \text{i.e., } dE_A = -dE_B \quad (\text{B1})$$

$$dV = dV_A + dV_B = 0 \quad \text{i.e., } dV_A = -dV_B \quad (\text{B2})$$

What about dS ? Rearranging the fundamental equation for the energy (Equation 12) gives

$$dS_A = \left(\frac{1}{T_A}\right) dE_A + \left(\frac{P_A}{T_A}\right) dV_A \quad (\text{B3})$$

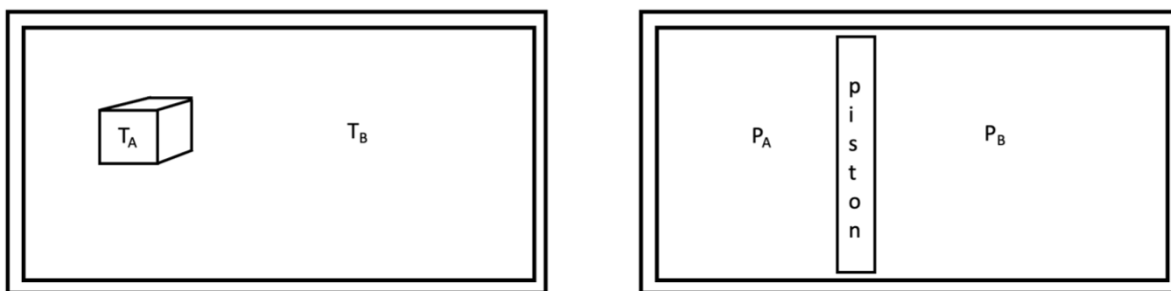
$$dS_B = \left(\frac{1}{T_B}\right) dE_B + \left(\frac{P_B}{T_B}\right) dV_B \quad (\text{B4})$$

Given Equations B1 and B2, we see that the sign of each of the terms in dS_B is opposite that of the corresponding term in dS_A no matter how the energy and volume are redistributed. However, we are interested in the overall change in entropy

$$\begin{aligned} dS &= dS_A + dS_B \\ &= \left[\left(\frac{1}{T_A}\right) - \left(\frac{1}{T_B}\right) \right] dE_A + \left[\left(\frac{P_A}{T_A}\right) - \left(\frac{P_B}{T_B}\right) \right] dV_A \end{aligned} \quad (\text{B5})$$

Familiar systems

The idea is to choose scenarios with which we have ample experience. The figure below shows two such cases. In one, the subsystems are initially at different temperatures, to make use of our experience that energy always moves from hotter to cooler objects. In the other, the subsystems are initially at different pressures, to make use of our experience that a region of lower pressure always gives up volume to a region of higher pressure. The following analyses show that both spontaneous processes are accompanied by an increase in the total entropy of the composite system, with one subsystem gaining more entropy than the other loses until overall equilibrium is achieved. The reader can verify that a similar analysis obtains the same result for a scenario in which the subsystems differ in the electrochemical potential for a constituent.



Two simple and familiar systems. Both are isolated (with their rigid, impermeable and insulating boundaries represented by double lines according to convention). Both have two subsystems that are initially at internal equilibrium. In one case, the two subsystems differ in temperature and the other in pressure.

The ΔT system

Suppose that the barrier between subsystems is rigid and impermeable (so $dV_A = 0$), but becomes thermally conducting (so $dE_A \neq 0$). Then

$$dS = \left[\left(\frac{1}{T_A} \right) - \left(\frac{1}{T_B} \right) \right] dE_A \quad (\text{B6})$$

and, specifically, with respect to time, t

$$\frac{dS}{dt} = \left[\left(\frac{1}{T_A} \right) - \left(\frac{1}{T_B} \right) \right] \frac{dE_A}{dt} \quad (\text{B7})$$

We know from experience that

$$\text{if } T_A = T_B, \text{ then } \left(\frac{dE_A}{dt} \right) = 0 \text{ and so } \left(\frac{dS}{dt} \right) = 0$$

$$\text{if } T_A < T_B, \text{ i.e., } \left[\left(\frac{1}{T_A} \right) - \left(\frac{1}{T_B} \right) \right] > 0 \text{ then } \left(\frac{dE_A}{dt} \right) > 0 \text{ and so } \left(\frac{dS}{dt} \right) > 0$$

$$\text{if } T_A > T_B, \text{ i.e., } \left[\left(\frac{1}{T_A} \right) - \left(\frac{1}{T_B} \right) \right] < 0 \text{ then } \left(\frac{dE_A}{dt} \right) < 0 \text{ and so } \left(\frac{dS}{dt} \right) > 0$$

In other words, our experience for this system says that

$$\frac{dS}{dt} > 0 \quad (\text{B8})$$

until the system reaches equilibrium where $T_A = T_B$, $(dE_A/dt) = 0$ and $(dS/dt) = 0$.

Notice that, according to Equation B6,

$$\frac{dS}{dE_A} = \left[\left(\frac{1}{T_A} \right) - \left(\frac{1}{T_B} \right) \right] = 0 \text{ at equilibrium } (T_A = T_B) \quad (\text{B9})$$

and

$$\frac{d^2S}{dE_A^2} = \frac{d \left(\frac{1}{T_A} \right)}{dE_A} - \frac{d \left(\frac{1}{T_B} \right)}{dE_A} < 0 \text{ for all } dE_A \quad (\text{B10})$$

Therefore, S has a maximum value at equilibrium ($T_A = T_B$) and no distribution of E between A and B has a higher S .

The ΔP system

Suppose that the barrier between subsystems is a perfect thermal conductor (so that $T_A = T_B = T$) and becomes free to move (so $dV_A \neq 0$). Then

$$dS = \left[\left(\frac{P_A}{T} \right) - \left(\frac{P_B}{T} \right) \right] dV_A \quad (\text{B11})$$

and specifically, with respect to time

$$\frac{dS}{dt} = \left[\left(\frac{P_A}{T} \right) - \left(\frac{P_B}{T} \right) \right] \frac{dV_A}{dt} \quad (\text{B12})$$

We know from experience that

$$\text{if } P_A = P_B, \text{ then } \left(\frac{dV_A}{dt} \right) = 0 \text{ and so } \left(\frac{dS}{dt} \right) = 0$$

$$\text{if } P_A < P_B, \text{ then } \left(\frac{dV_A}{dt} \right) < 0 \text{ and so } \left(\frac{dS}{dt} \right) > 0$$

$$\text{if } P_A > P_B, \text{ then } \left(\frac{dV_A}{dt} \right) > 0 \text{ and so } \left(\frac{dS}{dt} \right) > 0$$

In other words, our experience for this system says that

$$\frac{dS}{dt} > 0 \quad (\text{B13})$$

until system reaches equilibrium where $P_A = P_B$, $(dV_A/dt) = 0$ and $(dS/dt) = 0$.

Notice that, according to Equation B11,

$$\frac{dS}{dV_A} = \left[\left(\frac{P_A}{T} \right) - \left(\frac{P_B}{T} \right) \right] = 0 \text{ at equilibrium } (P_A = P_B) \quad (\text{B14})$$

and

$$\frac{d^2S}{dV_A^2} = \frac{d\left(\frac{P_A}{T}\right)}{dV_A} - \frac{d\left(\frac{P_B}{T}\right)}{dV_A} < 0 \text{ for all } dV_A \quad (\text{B15})$$

Therefore, S has a maximum value at equilibrium ($P_A = P_B$) and no distribution of V between A and B has a higher S .

Generalizing from the above examples, with no known counter-examples

In an isolated system, S increases until it attains its maximum possible value with respect to all available "degrees of freedom".

Notice that, while the entropy of the entire isolated system increases, the entropy of a subsystem can decrease. However, a local decrease in entropy always occurs at the expense of a greater increase in entropy elsewhere. This is especially relevant to biological growth and differentiation.

Notice also that, while the total energy in the system remains constant, one subsystem is initially capable of doing work on the other and finally is not. In other words, in the course of redistributing the energy, its availability to do work has been degraded.

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