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The law of entropy increase for bodies in mutual thermal contact

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The law of entropy increase for bodies in mutual thermal contact may be argued using the fact that the final temperature in the thermal process is higher than the final temperature in a reversible process for work extraction.
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When two bodies at unequal temperatures, $T_1 > T_2$, are put in mutual thermal contact, it is observed that the hot body cools down and the cold body warms up. The process continues until the two bodies reach a common temperature (T_F), which lies somewhere between the two initial temperatures: $T_1 > T_F > T_2$. The process is irreversible, implying that the total entropy ($\mathcal{S}$) of the two bodies increases in the process. Since entropy is a state function, the standard calculation of the entropy change in each body is performed by choosing any convenient reversible path that connects the initial and final equilibrium states of each body and applying the Clausius formula, $\Delta\mathcal{S}_i = \int dQ_i/T$, where $i = 1, 2$. For a reversible heat transfer, $dQ_i = C_i\,dT$, where the heat capacity $C_i > 0$ is, in general, a function of the temperature of the body and is process dependent. The total change in entropy is the sum of changes for the individual bodies, given by

$$\Delta\mathcal{S} = \int_{T_1}^{T_F} \frac{C_1 dT}{T} + \int_{T_2}^{T_F} \frac{C_2 dT}{T}, \tag{1}$$

where $\Delta\mathcal{S}_1 = \int_{T_1}^{T_F} C_1 dT/T < 0$, since $T_F < T_1$, and $\Delta\mathcal{S}_2 = \int_{T_2}^{T_F} C_2 dT/T > 0$, since $T_F > T_2$. Thus, the second-law inequality, $\Delta\mathcal{S} > 0$, is usually derived for this process by an explicit evaluation of the entropy changes while assuming a specific functional form for $C_i(T)$.[1] Even though one term is negative in the above, the sum of the two terms is positive. In this article, we show that $\Delta\mathcal{S} > 0$ may be argued from the fact that T_F is greater than the final common temperature T_f that would be reached via a reversible work extraction process—a fact which itself derives from the positivity of the heat capacity of each body.

As a concrete example, consider the case of two bodies with constant volumes and fixed heat capacities C_1 and C_2, for which we obtain[1]

$$\Delta\mathcal{S} = C_1 \ln\frac{T_F}{T_1} + C_2 \ln\frac{T_F}{T_2}, \tag{2}$$

where the final temperature, obtained from energy conservation, is $T_F = \alpha T_1 + (1-\alpha)T_2$, with $\alpha = C_1/(C_1 + C_2)$, satisfying $0 \le \alpha \le 1$. The above expression for the entropy change can be rearranged into the form

$$\Delta\mathcal{S} = (C_1 + C_2)\ln\left(\frac{\alpha T_1 + (1-\alpha)T_2}{T_1^{\alpha} T_2^{1-\alpha}}\right). \tag{3}$$

In this case, the proof of the inequality $\Delta\mathcal{S} > 0$ rests on the inequality between weighted arithmetic and geometric means, given by $\alpha T_1 + (1-\alpha)T_2 > T_1^{\alpha}T_2^{1-\alpha}$, for $T_1 \ne T_2$. There has been previous discussion around this apparent correspondence between physical laws and mathematical facts such as these inequalities.[2–11] However, the fact that one of the means in the above comparison, $T_1^{\alpha}T_2^{1-\alpha}$, is also the final common temperature of the two bodies when subjected to the process of reversible work extraction, seems to have escaped attention in the literature so far. More precisely, consider a reversible process that extracts work from the two bodies initially at temperatures T_1 and T_2.[1,12,13] This may be achieved by introducing a heat engine and running infinitesimal, reversible heat cycles that gradually reduce the temperature difference between the two bodies, until the two bodies obtain a common temperature T_f.[14] Now, T_f is determined by the reversibility condition: $C_1 \ln(T_f/T_1) + C_2 \ln(T_f/T_2) = 0$, yielding $T_f = T_1^{\alpha}T_2^{1-\alpha}$. So, Eq. (3) may be reexpressed as $\Delta\mathcal{S} = (C_1 + C_2)\ln(T_F/T_f)$. Therefore, we can say that the condition $T_F > T_f$ directly implies $\Delta\mathcal{S} > 0$. We argue below that $T_F > T_f$ holds not only for the case with algebraic means but also in general.

One may wonder, why does T_f figure in the expression for the entropy change in a thermal process? Actually, this suggests a suitable reversible path by which we can bring our initial two-body system to the final state at temperature T_F, and which also clarifies that $T_F > T_f$. The alternate path consists of two steps. In the first step, we bring the two bodies to the common temperature T_f by a reversible process, as described above. In the second step, an amount of heat—equal to the total work extracted above—is delivered to the two bodies, bringing them back at the initial total energy, but raising their common temperature to T_F. The temperature increases, because the heat capacity of each body is defined to be positive. Since energy in the form of heat is added to the system, so we also expect that the total entropy of the two bodies shows an increase. This line of reasoning is, expectedly, more palatable to the students compared to a plain application of the Clausius formula.[15]

In conclusion, many previous derivations of the second-law in a thermal equilibration process rely on the use of inequalities between algebraic means (see also Ref. 16). However, as we have seen above, the law of entropy increase follows owing to the reason that the final temperature reached for the thermal process is higher than the final temperature in a reversible process for work extraction. The necessary and sufficient condition for the above proof of the second law is the positivity of the heat capacity of individual bodies, which leads to the condition $T_F > T_f$.

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[14]The envisaged reversible step requires the presence of a heat engine, a reversible work source, and a set of auxiliary heat reservoirs. To visualize one such infinitesimal heat cycle—say, the first one—we have prepared the two bodies in initial states using reservoirs at temperatures T_1 and T_2. Now, assume that we have another pair of reservoirs, which differ from the initial pair by infinitesimally different temperatures, denoted as $T_1 - \delta T_1$ and $T_2 + \delta T_2$, where $\delta T_i > 0$. Now, an infinitesimal amount of heat dQ_1 is reversibly transferred from the hot body to the reservoir at $T_1 - \delta T_1$, a reversible heat cycle is run, which outputs work dW and rejects heat $dQ_2 = dQ_1 - dW$ to the reservoir at $T_2 + \delta T_2$. This heat is then reversibly transferred to the cold body at T_2. In this whole process, the engine and the auxilliary reservoirs undergo a reversible process, so their total change in entropy is zero. As a consequence, the sum of the entropy changes in the bodies is also zero. Furthermore, the temperature of the hot body is reduced to $T_1 - \delta T_1$ and that of cold body rises to $T_2 + \delta T_2$, thus decreasing the difference between their temperatures. The sequence of cycles is repeated using heat reservoirs at appropriate temperatures, until the two bodies arrive at a common temperature T_f.

[15]The procedure is easily extended to the case of n bodies at initial temperatures $\{T_i | i = 1, 2, \ldots, n\}$ and heat capacities $C_i(T) > 0$. In this case, the net entropy change in the *n bodies* during the proposed alternate process is expressed as $\Delta S = \sum_{i=1}^{n} \int_{T_i}^{T_f} (C_i(T)/T) dT + \sum_{i=1}^{n} \int_{T_f}^{T_F} (C_i(T)/T) dT$. The first sum vanishes due to the reversible work extraction step. Thus, the total entropy change is simply due to heat transfer to the collective system in the second step. Each integral in the second sum contributes positively, since $T_F > T_f$.

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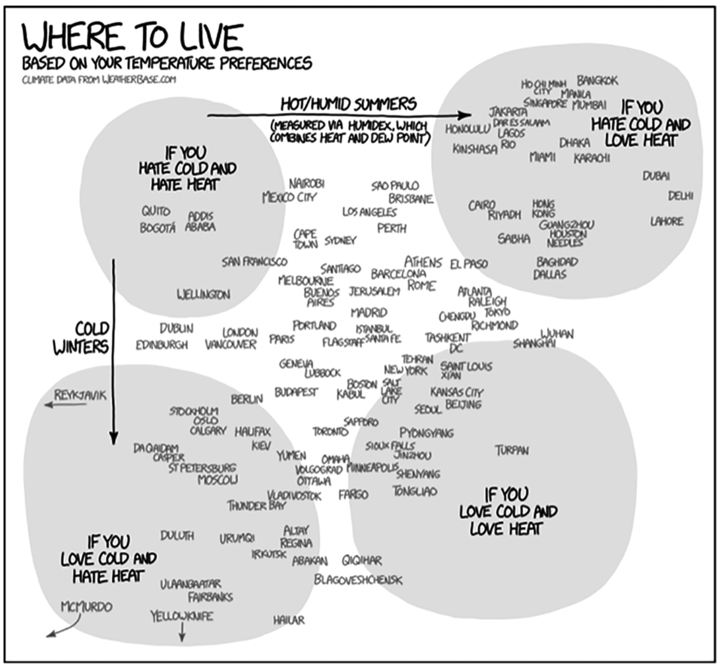

There's a supposed Mark Twain quote, "The coldest winter I ever spent was a summer in San Francisco." It isn't really by Mark Twain, but I don't know who said it–I just know they've never been to McMurdo Station. (Source: https://xkcd.com/1916/)

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