Entropy Generation in the Merging of Two Ideal Gases

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1 Problem

Show that positive entropy is generated when two volumes of ideal gases with different initial temperatures are merged in two different ways:

1. The volumes are placed in thermal contact, but the gases remain in their original volumes.

2. The partition between the two volumes is removed and the gases mix.

This problem was suggested by Julien Scordia, and is based on prob. I.4 of [1].

2 Solution

The two initial volumes V_i each contain n_i molecules of ideal gases of heat capacities $C_i k$ per molecule at initial temperatures T_i, where k is Boltzmann's constants, and say, $T_1 > T_2$. The total energy in the system is,

$$U = n_1 C_1 k T_1 + n_2 C_2 k T_2. \tag{1}$$

Assuming that the system under consideration is thermally isolated from the rest of the Universe, this energy is conserved in both processes, and in both cases the final temperature T is related by,

$$n_1 C_1 T_1 + n_2 C_2 T_2 = (n_1 C_1 + n_2 C_2) T, \tag{2}$$

$$T = \frac{n_1 C_1}{n_1 C_1 + n_2 C_2} T_1 + \frac{n_2 C_2}{n_1 C_1 + n_2 C_2} T_2. \tag{3}$$

Both processes are irreversible, but since entropy is a state function, we can compute the change in entropy of each gas by imagining reversible processes that lead to the same final state (of that gas). The total entropy change is, of course, the sum of the entropy changes of the two gases.

2.1 Equilibration without Change in the Volumes

In this case we imagine that each gas changes its temperature at constant volume as the result of reversible heat flow to a sequence of external reservoirs with all intermediate temperatures.[1] The reversible entropy change of gas i can now be written as,

$$\Delta S_i = \int \frac{dQ_i}{T} = n_i C_i k \int \frac{dT}{T} = n_i C_i k \ln \frac{T}{T_i}, \tag{4}$$

[1] A complicated set of thermal switches is required to carry out this sequence of heat transfers. That is while the irreversible equilibration of the temperature occurs "naturally", an extremely intricate scenario is required for the temperature changes to be a reversible.

and the total entropy change is,

$$\Delta S = n_1 C_1 k \ln \frac{T}{T_1} + n_2 C_2 k \ln \frac{T}{T_2}\,. \tag{5}$$

We expect that the total entropy change in the system of volumes 1 and 2 is positive (except for the trivial case that $T_1 = T_2 = T$), as the equilibration of the temperatures is irreversible when these volumes are in isolation.[2] However, $\ln T/T_1$ is negative, so it is not immediately obvious that ΔS of eq. (5) is positive.

We define $a_i = n_i C_i/(n_1 C_1 + n_2 C_2)$, such that $a_1 + a_2 = 1$ and eq. (5) can be rewritten as,

$$\frac{\Delta S}{n_1 C_1 k + n_2 C_2 k} = a_1 \ln \frac{T}{T_1} + a_2 \ln \frac{T}{T_2} = \ln T - a_1 \ln T_1 - a_2 \ln T_2. \tag{6}$$

Hence, ΔS is positive if,

$$T = a_1 T_1 + a_2 T_2 > T_1^{a_1} T_2^{a_2} \qquad (a_1 + a_2 = 1). \tag{7}$$

For the special case that $a_1 = a_2 = 1/2$ this follows from the fact that unless $T_1 = T_2$,

$$\left(\frac{T_1 + T_2}{2}\right)^2 - \sqrt{T_1 T_2}^{\,2} = \left(\frac{T_1 - T_2}{2}\right)^2 > 0. \tag{8}$$

The general case (which for m volumes of m gases at initial temperatures T_i leads to $\Delta S > 0$ if $a_1 T_1 + a_2 T_2 + \cdots + a_m T_m > T_1^{a_1} T_2^{a_2} \cdots T_m^{a_m}$ when $a_1 + a_2 + \cdots + a_m = 1$) is an example of an inequality attributed to MacLaurin (≈ 1740).[3]

2.2 Equilibration by Mixing

In case the two gases, initially in separate volumes, mix together into a single final volume V, the entropy change is the sum of that associated with each gas expanding freely from its initial volume V_i to V while its temperature changes from T_i to T.

We compute these entropy changes by imagining the evolution occurs reversibly in two steps, first arriving reversibly at the final temperature T with no change in volume, and then the volumes expanding reversibly at constant temperature T. The entropy change of the first step is given in eq. (5). In the second step (where the energies of the gases again remain constant),

$$dU = 0 = dQ - dW, \qquad dQ = dW = P dV = \frac{nkT dV}{V}\,, \tag{9}$$

for an ideal gas, where k is Boltzmann's constant. Hence, the entropy changes $\Delta S_i'$ in the second step are given by,

$$\Delta S_i' = \int \frac{dQ_i}{T} = n_i k \int \frac{dV}{V} = n_i k \ln \frac{V_1 + V_2}{V_i} > 0. \tag{10}$$

[2]The total entropy change is zero for these systems plus the sequence of auxiliary systems that would permit a reversible transformation.

[3]See, for example, secs. 2.5-6 of [2]. If one accepts the second law of thermodynamics, it can be regarded as "proof" of MacLaurin's inequality.

Since the sum of the entropy changes of the two volumes is positive in the second step, the total entropy change is positive (even if $T_1 = T_2$),[4]

$$\Delta S = n_1 C_1 k \ln \frac{T}{T_1} + n_2 C_2 k \ln \frac{T}{T_2} + n_1 k \ln \frac{V_1 + V_2}{V_1} + n_2 k \ln \frac{V_1 + V_2}{V_2} > 0. \tag{11}$$

2.3 Mixing at Constant Pressure

A variant on the case of mixing of the two gases is to suppose that their initial pressures are the same.[5] If the two gases are isolated from the rest of the Universe, the result (11) holds with the additional constraint that,

$$P = \frac{n_1 k T_1}{V_1} = \frac{n_2 k T_2}{V_2}, \qquad V_2 = \frac{n_2 T_2}{n_1 T_1} V_1, \qquad V = V_1 + V_2 = V_1 \frac{n_1 T_1 + n_2 T_2}{n_1 T_1}. \tag{12}$$

The final pressure is, recalling eq. (3),

$$P_{\text{final}} = \frac{(n_1 + n_2) k T}{V} = \frac{n_1 + n_2}{n_1 T_1 + n_2 T_2} \frac{(n_1 C_1 T_1 + n_2 C_2 T_2)}{(n_1 C_1 + n_2 C_2)} \frac{n_1 k T_1}{V_1}, \tag{13}$$

which equals the initial pressure P if $C_1 = C_2$ (identical gases) but not in general.

The variant as posed in [4] adds the assumption of identical gases, in which case $P_{\text{final}} = P$, and the following analysis holds.

We can compute the entropy change by considering a single step in which each gas changes its temperature (and its volume) reversibly at constant pressure P (by interaction with a sequence of auxiliary systems of fixed pressure and intermediate temperatures). During these reversible transformations,

$$dU_i = n_i C k\, dT_i = dQ_i - P dV_i = dQ_i - n_i k\, dT_i, \qquad dS_i = \frac{dQ_i}{T_i} = \frac{n_i (1 + C) k\, dT_i}{T_i}, \tag{14}$$

$$\Delta S = n_1 (1 + C) k \ln \frac{T}{T_1} + n_2 (1 + C) k \ln \frac{T}{T_2}. \tag{15}$$

We define $b_i = n_i/(n_1 + n_2)$, such that $b_1 + b_2 = 1$, $T = b_1 T_1 + b_2 T_2$ and eq. (15) can be rewritten as,

$$\frac{\Delta S}{(n_1 + n_2)(1 + C) k} = b_1 \ln \frac{T}{T_1} + b_2 \ln \frac{T}{T_2} = \ln T - b_1 \ln T_1 - b_2 \ln T_2. \tag{16}$$

Hence, ΔS is positive when $T_1 \neq T_2$ according to the version of MacLaurin's inequality,

$$T = b_1 T_1 + b_2 T_2 > T_1^{b_1} T_2^{b_2} \qquad (b_1 + b_2 = 1). \tag{17}$$

[4]The case with $T_1 = T_2$ is posed as prob. 4-54 in [3].

[5]This version is posed as prob. 7.7 in [4].

References

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[3] S.B. Cahn, G.D. Mahan and B.E. Nadgorny, *A Guide to Physics Problems, Part 2* (Plenum Press, 1997), http://kirkmcd.princeton.edu/examples/statmech/cahn_74_part2.pdf

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