The thermodynamic equilibrium of gas in a box divided by a piston

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Abstract

The equilibrium conditions of a system consisting of a box with gas divided by a piston are revised. The apparent indetermination of the problem is solved by explicitly imposing the constancy of the internal energy when the Entropy Maximum Principle is applied. The equality of the pressures is naturally concluded from this principle when the piston is allowed to spontaneously move. The application of the Energy Minimum Principle is also revised. A new parameter is introduced for calculating the evolution of systems exchanging volume and/or particles.

I. Introduction

Establishing the equilibrium conditions for a system consisting of a gas-containing box divided by an adiabatic piston from the thermodynamic principles of has been an elusive problem.\cite{1,2,3} It is clear that the mechanical equilibrium is reached when the pressures in both sides are equal to each other. However, how to extract this condition from the Entropy Maximum Principle has proven to be confusing. Some authors have claimed that the problem is indeterminate.\cite{1,4,5} Some others have even got to the (wrong) conclusion that the equilibrium is reached when the ratio of the pressure to the temperature $P/T$ is the parameter that should be equal in both sides.\cite{6,7} Many other authors also arrived to this same conclusion but adding the statement that the temperatures should also be equal to each other, thus effectively considering only the case of a diathermal piston wall.\cite{4,8,9}

In 1969 Curzon treated this problem and tried to conclude the equality of the pressures from the maximization of the entropy.\cite{10} This work is frequently referred as the appropriate approach.\cite{1,3,11} However, the argument employed assumes that the increase of entropy is identically equal to zero, which, as discussed below and pointed out earlier,\cite{12} is equivalent to assume (but not to show) that the pressures are equal. It also assumes an incorrect relationship between the change on volume and the change on internal energy.

There is a large amount of related literature dealing with alternative mechanisms of energy transport across an insulating piston from one side to the other which are at equal pressures but different temperatures.\cite{13,14,15,16} It is interesting that, for frictionless systems, a macroscopic transfer of energy between the two sides is predicted even if the piston wall is perfectly isolating. This transfer is originated by the thermal fluctuations on the movement of the piston, which in turn are caused by the collisions of the gas particles with the piston. In the predicted final state the temperatures in both sides are equal to each other. This mechanism of energy transfer is not going to be considered in this paper because the effect is only appreciable for frictionless and very light pistons, and in very long time-scales. In real systems the friction is not zero and its presence would right away damp the transfer of energy through this means.
One of the main issues discussed in this paper is the deduction of the conditions for thermodynamic equilibrium from the Entropy Maximum Principle, specifically for the case in which volume can be interchanged and the piston is insulating. It can be directly shown that the change of total entropy $S$ when energy, volume, and particles (of type $a$) can be interchanged between the two sides of the box is given by

$$\text{Eq 1} \quad dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left( \frac{\mu_{a,1}}{T_1} - \frac{\mu_{a,2}}{T_2} \right) dN_{a,1},$$

where $U_i$, $T_i$, $P_i$, $V_i$, $\mu_{a,i}$, and $N_{a,i}$ are the internal energy, temperature, pressure, volume, chemical potential of specie $a$, and number of particles of specie $a$ for side $i$ ($i=1,2$). The system is assumed isolated ($dU_1 + dU_2 = 0$), with constant total volume ($dV_1 + dV_2 = 0$), and with constant number of particles ($dN_{a,1} + dN_{a,2} = 0$). This equation is employed in most of the approaches trying to extract the equilibrium conditions from the Entropy Maximum Principle. In fact, from Equation 1 it is indeed possible to extract the condition of thermal equilibrium. By removing the constraint of heat flow (diathermal piston), $dU_1$ could be made different from zero and at the same time keeping the volume and number of particles fixed in each side ($dV_1 = 0$ and $dN_{a,1} = 0$). Since in equilibrium $S$ is maximum ($dS = 0$), then the temperatures should be equal when the piston wall is diathermal.

Deducing the other condition for equilibrium is not as straightforward. Part of the existing confusion in the literature arises when the condition of mechanical equilibrium is tried to be extracted by making zero the coefficient of $dV_1$. It should be stressed that a change on $V_1$ implies a change on $U_1$. Since they are not independent, the whole combination $(1/T_1 - 1/T_2)dU_1 + (P_1/T_1 - P_2/T_2)dV_1$ should instead be set to zero. It is indeed possible to extract the equality of the pressures from the combined condition. This is properly done in Section II.

In Sections IV and VI it is discussed the phrasing of the Entropy Maximum and Energy Minimum Principles. The extraction of the equilibrium conditions by employing the Energy Minimum Principle is discussed in Section V. The application of the proposed approach to the solution of some simple problems is described in Section VII.

II. The equilibrium conditions obtained from the Entropy Maximum Principle

Another part of the confusion is the wide-spread error of applying the Entropy Maximum Principle without guaranteeing that the total internal energy is kept constant. When quasistatic movements of the piston are allowed, it is often assumed that the change on internal energy in each side is equal to $-P_i dV_i$ ($i=1,2$). If this were the case, the total energy would not be constant since the change on the total energy due to a displacement of the piston would be $dW = -(P_1 - P_2)dV_1$ ($P_1 \geq P_2$ will be assumed throughout the whole treatment). The Entropy Maximum Principle is only valid when the total energy is constant. In truly isolated system, this work is converted into some other form of energy, causing an increase of the internal energy of the system or/and an increase on the kinetic energy of the piston or the fluid. The treatment in this paper is restricted to quasistatic processes in which the kinetic energy is negligible. Since
this is the case for states close to equilibrium, this restriction does not prevent obtaining the conditions for thermodynamic equilibrium from the Entropy Maximum Principle, which is the main purpose of the work presented in this paper.

By means of friction, the displacement of the piston causes a conversion of the work into an increment of the internal energy of the system in the form of disorganized energy (or thermal energy). That conversion of work into thermal energy is an irreversible process whose result is an increment on the entropy of the same amount as if an equivalent amount of heat \(dQ' = (P_1 - P_2)dV_1\) had flowed in. This thermal energy ends up in some part of the system which, besides the gas, is also composed by the wall of the container and the piston. If a fraction \(\chi_1\) of \(dQ'\) ends up in side 1, and the rest \(\chi_2 = 1 - \chi_1\) end up in side 2, the associated increment in entropy, \(dS_W\), is given by

\[
\text{Eq 2} \quad dS_W = \frac{\chi_1 dQ'}{T_1} + \frac{\chi_2 dQ'}{T_2}.
\]

A more general approach could be easily introduced by considering a temperature field \(T(r)\). \(T(r)\) is equal to \(T_1\) for \(r\) belonging to side 1, and equal to \(T_2\) for \(r\) belonging to side 2. By considering the temperature field, the possibility of intermediate temperatures within the wall of the piston would also be considered. Then, in general, the increment on entropy is given by

\[
\text{Eq 3} \quad dS_W = \frac{(P_1 - P_2)dV_1}{T(r)} \int \chi(r) d^3r = (P_1 - P_2)dV_1 \int \frac{\chi(r) d^3r}{T(r)},
\]

where \(\chi(r) d^3r\) is the fraction of \(dQ'\) ending up at the volume \(d^3r\) around \(r\); it is normalized to 1. \(\chi_1\) (\(\chi_2\)) is equal to the integral of \(\chi(r)\) over the region \(R_1\) (\(R_2\)) where the temperature is equal to \(T_1\) (\(T_2\)). The integration is done over the whole system, including the walls and the piston. The function \(\chi(r)\) depends on the details of the quasistatic process and of the system.

The integral quantifies how an infinitesimal amount of energy \((P_1 - P_2)dV_1\) is distributed within the system in a quasistatic process. This distribution causes infinitesimal increments on the temperature along the system; they do not contribute to the generation of entropy to first infinitesimal order.

To keep the treatment general, heat exchange between the two sides will also be allowed. The associated increment on entropy is

\[
\text{Eq 4} \quad dS_Q = \frac{dQ_{2\rightarrow1}}{T_1} + \frac{dQ_{1\rightarrow2}}{T_2},
\]

where \(dQ_{2\rightarrow1}\) is the heat transferred into side 1 from side 2 (e.g., through the piston wall), and \(dQ_{1\rightarrow2}\) is the opposite. By definition, \(dQ_{2\rightarrow1} + dQ_{1\rightarrow2} = 0\). The total change of entropy is obtained by adding the contributions from Equations 3 and 4:

\[
\text{Eq 5} \quad dS = dS_W + dS_Q = \left(1 - \frac{1}{T_1} \right) dQ_{2\rightarrow1} + \int \frac{\chi(r) d^3r}{T(r)} \times (P_1 - P_2)dV_1.
\]
Note that the factor containing $\chi$ is never zero or negative because $\chi$ (and the temperature) is always positive. Equation 5 applies regardless of whichever is the mechanism of redistribution of the energy. It also applies regarding the existence of regions within the piston wall at intermediate temperatures. Still, the actual value of $dS$ depends on the function $\chi(r)$. Thus, Equation 5 is not predictive unless a model for this function is provided. This clearly illustrates that the equilibrium final state might depend on the details of the process. This is in apparent contradiction to statements frequently found in textbooks that the final state is independent of the path to equilibrium. If the piston is thermally isolating, the final equilibrium state will indeed depend on how the energy $dQ'$ is distributed between the two sides. It also illustrates that such details enters into the calculation through the function $\chi(r)$.

Since the total internal energy has been kept constant, it is now possible to apply the Entropy Maximum Principle. It should be stressed that the amount of heat transferred between the two sides ($dQ_{2\to1}$) and the exchange of volume ($dV_1$) are independent from each other. They area controlled by independent constraints. This independence makes possible to extract the thermodynamic equilibrium conditions. Since at equilibrium $dS=0$, then either the temperatures are equal or the heat transfer is not allowed ($dQ_{2\to1}=0$), and either the pressures are equal or the exchange of volume is not allowed ($dV_1=0$). As a conclusion,

when the piston is allowed to move, the equality of the pressures is an equilibrium condition naturally obtained from the Entropy Maximum Principle.

This conclusion is general for quasistatic processes since it holds regardless whether the system can be divided into two sides (one at temperature $T_1$ and the other at $T_2$) or the boundary between the two sides at intermediate temperatures has a non-neglecting heat capacity and the integral of Equation 5 has to include this boundary (the integral is over the whole system, including the piston and the walls). It is also important to stress that the entropy increases precisely because the available energy (work) is converted into disorganized internal energy (“heat”). In fact, the Entropy Maximum Principle of thermodynamics is sometimes stated as\cite{18}

If a closed system is at some instant in a non-equilibrium macroscopic state, the most probable consequence at later instants is a steady increase in the entropy of the system.

and\cite{7}

The spontaneous tendency of a system to go towards equilibrium cannot be reversed without at the same time changing some organized energy, work, into disorganized energy, heat.

In the same way, it can be shown that, when the exchange of particles of some type (e.g., type a) is allowed, the change on entropy is given by

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dQ_{2\to1} + \int \frac{\chi(r) d^3r}{T(r)} \times (P_1 - P_2) dV_1$$

\textbf{Eq 6}

$$- \int \frac{\chi(r) d^3r}{T(r)} \times (\mu_{a,1} - \mu_{a,2}) dN_{a,1}$$
Thus, it can be stated that

when particle exchange is allowed, the equality of the chemical potentials is also a consequence of the Entropy Maximum Principle.

It is important to emphasize this because it has wrongly been claimed that the chemical equilibrium (when the flow of particle of type \( a \) is allowed) is achieved when the ratio of the chemical potential to the temperature (\( \mu_a / T \)) is the same in both sides.\(^7\) In any case, the parameter \( \chi \) should take part in the calculation of the evolution of systems exchanging particles.

### III. Discussion of previous approaches

Apparently, it was Herbert Callen who first raised the question of deriving the thermodynamic equilibrium conditions of a box divided by a piston from the Entropy Maximum Principle.\(^4\) His conclusion was that the problem was indeterminate when the piston wall is adiabatic. His error consisted in treating the differentials in Equation 1 as independent from each other. In this way he derived the incorrect equation

\[
\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}} = 0 \quad \text{(Equation 2.54 of the Second Edition.)} \]

Since the result is obviously incorrect when the temperatures are different, he stated that the equation is valid only when the temperatures are the same, and that the treatment is valid only for diathermic piston walls. Other authors of text books kept the validity of the equation even when the temperatures are different, and reached to the conclusion that \( P/T \) is equal in both sides in equilibrium.\(^6,7\)

As mentioned above, Curzon treatment\(^10\) is commonly regarded as the correct approach.\(^1,3,11\) In the light of the previous discussion it is straightforward to show that this is not the case. The first error made in his treatment is applying the Entropy Maximum Principle to each side separately. This is fundamental to his approach since it is used to derive his Equations 10 (\( dS_1 \geq 0 \)) and 11 (\( dS_2 \geq 0 \)), which are the core of his argument. This is not correct because the principle can only be applied when the internal energy of each subsystem is constant. Their energies are not constant because they can, at least, exchange energy in the form of work. In addition, as shown in Section II, the exchange of work between the two sides implies the generation of internal energy that ends up in the form of heat. That is, the subsystems cannot be thermally isolated if work exchange is allowed and the total energy of the combined system is to remain constant.

By employing his Equations 10 and 11, and using that \( dS = 0 \) in equilibrium, he concludes that \( dS_1 = dS_2 = 0 \) (Equation 12). In the following derivation he only employs that \( dS_1 = 0 \). Since the latter equation was derived under wrong procedures, it could be considered as an assumption. Assuming that \( dS_1 = 0 \) has some consequences. First of all, it is equivalent to assume that \( dU_1 = -P_1 dV_1 \) (Equation 13). Since it is also assumed that \( dU_1 = -dU_2 \), this implies that \( dU_2 = P_1 dV_1 \). On the other hand, since \( dU_2 = -P_2 dV_2 - T_2 dS_2 \), then \( -T_2 dS_2 = (P_1 - P_2) dV_1 \). This implies that the whole energy \( dQ' = (P_1 - P_2) dV_1 \) is delivered to side 2. This is the particular case in which \( \chi_1 = 0 \) and \( \chi_2 = 1 \) in the Equation 2 shown in Section II. Curzon treatment is, then, equivalent to that presented in Section II only for the case in which the whole energy \( dQ' = (P_1 - P_2) dV_1 \) is acquired by one of the sides. There is no simple way to assure or control that the whole energy \( dQ' \) ends up in only one side. In addition to not being general, it wrongly employs the Entropy Maximum Principle to not isolated systems.
In a following paper of Curzon and Leff about this topic,\textsuperscript{11} they derive the equilibrium conditions by making a different and more serious mistake. To derive their Equation 8 they assume that $dQ_1 = dQ_2 = 0$. Since, as shown above, $dQ_1 = dQ_2 \rightarrow 1 + \chi_1 dQ \rightarrow 1 = dQ_2 \rightarrow 1 + \chi_1 (P_1 - P_2) dV_1$, and $dQ_2 \rightarrow 1 = 0$ for adiabatic pistons, assuming that $dQ_1 = 0$ is equivalent to assume that $\chi_1 (P_1 - P_2) dV_1 = 0$. Then, by assuming that $dQ_1 = dQ_2 = 0$ they in fact assumed that $P_1 = P_2$. Thus, their argument for deriving the mechanical equilibrium conditions is circular.

IV. A note about the statement of the Entropy Maximum Principle

The precise way in which the Entropy Maximum Principle is enunciated can contribute to the confusion described in Section I. Some authors make special emphasis on internal parameters. Examples are the statements employed by Callen:\textsuperscript{4}

\begin{enumerate}
\item \textit{the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states,}
\item \textit{the equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.}
\end{enumerate}

It is clear that $V_1$ and $N_{a,1}$ qualify as extensive parameters. However, the quantity $Q_2 \rightarrow 1$ associated to the other differential $dQ_2 \rightarrow 1$ in Eq 6 does not. Since $dQ_2 \rightarrow 1$ represents a variation, there is no discrepancy if the Gibbs text is employed instead:\textsuperscript{17}

\textit{For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.}

A more operative statement which is equivalent to the previous one is the following:

\textit{The spontaneous changes in an isolated system when a constraint is removed are such that the entropy increases, reaching a maximum value at equilibrium.}

The changes of the system are represented by $dQ_2 \rightarrow 1$, $dV_1$, and $dN_{a,1}$. Away from equilibrium, their signs are such that the total entropy increases. For example, if $T_2 > T_1$ the sign of $dQ_2 \rightarrow 1$ should be positive to cause an increase on the total entropy. The exchange of heat, volume, and particles are the result of the removal of independent constrains. Experimentally, it is clear how each one could be independently removed.

To illustrate how the use of Callen’s statement of the Entropy Maximum Principle could lead to wrong conclusions, Equation 5 will be written in terms of differentials of internal variables. The change on entropy on side 1 could be written as

$$dS_1 = (P_1 - P_2) dV_1 \int_{K_1} \frac{\chi(r) d^3r}{T(r)} + \frac{dQ_2 \rightarrow 1}{T_1} = \frac{\chi_1 (P_1 - P_2) dV_1 + dQ_2 \rightarrow 1}{T_1}.$$
then, if the temperature at \( R_1 \) is constant and equal to \( T_1 \), we have that

\[
dQ_{2 \rightarrow 1} = T_1 \, dS_1 + \chi_1 \left( P_1 - P_2 \right) dV_1.
\]

By substituting this into Equation 5 then we could find that

**Eq 7**  
\[
dS = \left( 1 - \frac{T_1}{T_2} \right) dS_1 + \frac{(P_1 - P_2)}{T_2} \, dV_1.
\]

Note that \( dS \) is not longer explicitly dependent on \( \chi_1 \); its dependence is implicit through \( dS_1 \).

If particle exchange is allowed, then

**Eq 8**  
\[
dS = \left( 1 - \frac{T_1}{T_2} \right) dS_1 + \frac{(P_1 - P_2)}{T_2} \, dV_1 - \frac{(\mu_{a,1} - \mu_{a,2})}{T_2} \, dN_{a,1}.
\]

In this way the differential on total entropy is written in term of the differentials of the internal parameters \( S_1, V_1, \) and \( N_{a,1} \). Although it is tempting to try to extract the equilibrium conditions from Eq 7 (or Eq 8), this cannot be done because the differentials \( dS_1 \) and \( dV_1 \) (and \( dN_{a,1} \)) are not independent from each other. Experimentally, they cannot be turned on and off independently by removing the appropriate constraints. As shown above, the adiabatic condition of the piston wall does not imply that \( dS_1 = 0 \). It is very important to note that Eq 7 does not imply that the change on total entropy caused by a change on \( V_1 \) is equal to \( (P_1 - P_2)/T_2 \, dV_1 \) since a change in \( V_1 \) causes a change on \( S_1 \) (\( dS_1 \) is in general different from zero, it depends on \( \chi_1 \), which is not controlled by the constrains).

This line of thought could be taken further down. If \( dS_1 \) is written in terms of \( dU_1 \), then it is possible to return to the expression

\[
dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \frac{P_1}{T_1} - \frac{P_2}{T_2} \, dV_1 - \left( \frac{\mu_{a,1}}{T_1} - \frac{\mu_{a,2}}{T_2} \right) \, dN_{a,1}.
\]

Since the differentials \( dU_1 \), \( dV_1 \), and \( dN_{a,1} \) cannot be turned on and off independently from each other by removing the appropriate constraints, the equilibrium principle under the removal of constraints does not imply that the coefficients could be independently set to zero. In fact, doing so would yield to wrong conclusions (such as that the mechanical equilibrium is reached when \( R_1/T_1 = P_2/T_2 \)). However, the terms could be rearranged as in Equation 6, where the differentials are actually independent from each other, and the correct equilibrium conditions could be found from the Entropy Maximum Principle.

**V. The equilibrium conditions obtained from the Energy Minimum Principle**

In Callen’s classic book of thermodynamics, the conditions of equilibrium of the system here in question are attempted to be extracted from the Energy Minimum Principle.\(^4\) However, it is not done properly. The error consisted of not assuring that the entropy remains constant. This is fundamental since the principle of minimum energy applies only when the total entropy is kept
constant. The quasistatic exchange of heat through the wall induces the following change on entropy

\[ Eq \ 9 \quad dS_{\text{exchange}} = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dQ_{2 \to 1}. \]

Since heat flows from the warm side to the cooler one, \( dS_{\text{exchange}} \) is greater than zero if the temperatures are different. Requiring that \( dS_{\text{exchange}} = 0 \) when heat exchange is allowed (\( dQ_{2 \to 1} \neq 0 \)) is equivalent to requiring that the temperatures are the same. That is, to require that \( dS_{\text{exchange}} = 0 \) is equivalent to require or assume that \( T_1 = T_2 \), but not to show that they have to be equal in equilibrium. This is the error made in the Callen’s approach, in which \( dS_{\text{exchange}} \) is assumed to be zero and then wrongly concluded that the equality of the temperatures was in fact demonstrated.

It is possible to show that the temperatures should be equal in equilibrium in the following way. To actually keep the entropy constant (when the temperatures are not equal and heat transfer is allowed) it is necessary to extract certain amount of heat (\( dQ' < 0 \)) to compensate for the increase on entropy caused by the exchange of heat (quantified in Equation 9). The associated change on entropy is

\[ Eq \ 10 \quad dS_{Q'} = \int dQ' \left( \frac{\zeta(r)}{T(r)} \right) dV = \left( \frac{\zeta_1}{T_1} + \frac{1 - \zeta_1}{T_2} \right) dQ', \]

where \( \zeta(r) d^3r \) is the fraction of \( dQ' \) extracted from the volume \( d^3r \) around \( r \). In the same train of arguments leading to Equation 2, \( \zeta_1 \) is the integral of \( \zeta(r) \) over the side 1 (\( R_1 \)). Then, the total change in entropy is the sum of the contributions from Equations 9 and 10

\[ dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dQ_{2 \to 1} + \left( \frac{\zeta_1}{T_1} + \frac{1 - \zeta_1}{T_2} \right) dQ'. \]

If the entropy is to be kept constant (\( dS = 0 \)), the amount of heat that should be extracted is

\[ dQ' = \frac{1}{\frac{\zeta_1}{T_1} + \frac{1 - \zeta_1}{T_2}} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) dQ_{2 \to 1}. \]

The factor containing \( \zeta_1 \) is always positive for \( 0 \leq \zeta_1 \leq 1 \). The total change on internal energy is then

\[ Eq \ 11 \quad dU = \frac{1}{\frac{\zeta_1}{T_1} + \frac{1 - \zeta_1}{T_2}} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) dQ_{2 \to 1} + (P_1 - P_2) dV_1 + (\mu_{a,1} - \mu_{a,2}) dN_{a,1}. \]

Although this expression is valid in general, the actual value of \( dU \) depends on the function \( \zeta(r) \). As in Equation 5, this equation is not predictive until a proper model for this function is
provided. It is important to notice that the final equilibrium state depends on the details of the system and process (quantified through $\zeta$).

Since this assures that the system evolves in a surface of constant entropy, the Energy Minimum Principle can now be applied. It is then direct to show that, in equilibrium, if heat exchange is allowed, the temperatures should be the same, and if volume is allowed to change, the pressures should be the same. In addition, if particle exchange is allowed, then in equilibrium the associated chemical potentials of both sides are equal to each other.

VI. A note about the statement of the Energy Minimum Principle

The way in which the Energy Minimum Principle is enunciated in Callen’s book\(^4\)

\begin{quote}
the equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy,
\end{quote}

also emphasizes on the minimization respect to internal parameters. This statement is not operative since $Q_{2 \rightarrow 1}$ is not an internal parameter, so it cannot be employed to extract the equilibrium conditions from Eq 11. There is no problem if Gibbs statement is employed:\(^{17}\)

\begin{quote}
For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive
\end{quote}

A more functional way to enunciate the Energy Minimum Principle which is consistent with the previous one is the following:

\begin{quote}
When a constraint is removed, the spontaneous changes not causing a variation on the total entropy of a system are such that the internal energy decreases, reaching a minimum value at equilibrium.
\end{quote}

VII. Solution to some special cases

The approaches used in Sections II and V are operative in the sense that they pave the way for the prediction of the final state, which is the main objective of thermodynamics. Some simple cases will be described. Since the final state depends on the parameter $\chi$, when the Entropy Maximum Principle is employed, or on $\zeta$, when the Energy Minimum Principle is employed, the solution of the problems involves an estimation of one of these parameter. In these examples the gas will be assumed as ideal and monatomic and the wall of the piston as adiabatic. For each side it holds that

\begin{equation}
\text{Eq 12} \quad p = \frac{2}{3} \frac{U}{V} \quad \text{and} \quad T = \frac{2}{3} \frac{U}{R N}.
\end{equation}

A. Perfect adiabatic subsystems

The simplest case is in which the work $-(P_1 - P_2) dV_1$ is not given back to the system in the form of internal energy or in any form. This could be achieved by employing an external machine that appropriates all this work. Given that the total entropy remains constant, it is possible to apply the Energy Minimum Principle to find the equilibrium conditions. Since no heat exchange is
going to be allowed, no heat has to be extracted \((dQ' = 0)\) and the parameter \(\zeta\) is irrelevant. In this case the entropy of each side is kept constant, thus \(dU_i = -P_i dV_i \) \((i = 1, 2)\). This equation could be solved to show that \(P_i V_i^{5/3} \) \((i = 1, 2)\) remains constant for each side (a known relation for adiabatic ideal gases). Since that total entropy remains constant, it is possible to apply the principle of minimum energy and to require that \(P_{1,f} = P_{2,f} \). It is straightforward to show that

\[ V_{1,f} = \frac{P_1^{3/5} V_1^{1,0}}{P_1^{3/5} V_1^{1,0} + P_2^{3/5} V_2^{2,0}} V_{\text{tot}}. \]

The final pressures, temperatures, and energies could then be calculated employing Equation 12.

**B. Slow piston (no oscillation)**

When the friction is large enough to prevent the acceleration of the piston, the work \(dW = -(P_1 - P_2) dV_1\) is completely transformed into internal energy. This work is initially transformed into an increment of the internal energy of the surfaces sliding against each other. By means of heat conduction, in quasistatic processes this energy end up somewhere in the system. If the heat capacity of the boundary is negligible, then

\[ dU_1 = \chi_1 (P_1 - P_2) dV_1 - P_1 dV_1. \]

\[ dU_2 = (1 - \chi_1)(P_1 - P_2) dV_1 + P_2 dV_1. \]

Since the total energy has been kept constant, it is possible to use the Entropy Maximum Principle and require that the final pressures are equal to each other. This system of equations (Equations 13) can be solved analytically if \(\chi_1\) is assumed to be constant. Since the expanding side gets first in contact with the surface heated by means of friction, a larger fraction of the energy \((P_1 - P_2) dV_1\) ends up in that side. To simplify the problem it is going to be assumed that all this energy is captured by the expanding side \((\chi_1 = 1\) for \(dV_1 > 0)\). In addition, the heat conductivity and capacity of the walls and of the piston will be assumed as negligible, so all the energy is incorporated into the gas of the expanding side. The walls and the piston will only play a role as a carrier of energy into the gas. For this particular case it is straightforward to show that the final volume of side two is given by

\[ V_{2,t} = \left( \frac{U_{2,0} V_{\text{tot}}}{U_{\text{tot}}} \right)^{2/5} V_{\text{tot}}^{3/5} 2,0. \]

The final pressures, temperatures, and energies could then be calculated employing the expressions in Equation 12.

This same problem is solved differently by Ferreira.\(^{19}\) To find the final state it is assumed that the final equilibrium position of the piston is the same as if the process had been adiabatic in both sides, exactly as in the previous example. To end up with the total final energy equal to the total initial energy, an appropriate amount of heat is then added to each side but maintaining the
pressures equal to each other during the heat-adding process and keeping the piston immobile. This is equivalent to assuming a constant value of $\chi_1$ equal to 0.5. The assumption is a good approximation when the piston oscillates many cycles before coming to rest since, in that case, each side corresponds to the expanding side about half of the time.

The advantage of introducing the parameter $\chi_1$ in the treatment of this problem is that it clearly shows that the final state depends on the details of the path to equilibrium, and that every path could be associated to a particular evolution of the function $\chi(r)$.

C. Oscillating piston

If the piston accelerates appreciably, its kinetic energy should be part of the energy balance. The approach of the previous example could be expanded to non-quasistatic processes under certain assumptions. As in the treatment by Ferreira, the oscillation of the piston could be approximately modeled by taking $\chi_1 = 0.5$ in Equations 13. A more general approach is described in this section. The equation of motion of the piston can be written as

$$\text{Eq 14} \quad \sigma A \frac{dv}{dt} = (P_1 - P_2)A - \kappa v,$$

where $\sigma$ is the surface density of the piston, $A$ is the area, $\kappa$ is the friction coefficient, and $v$ is the speed of the piston. The energy converted into internal energy as the piston moves is $\kappa v dx$, which is always positive ($dx$ is the piston displacement, with $dV_1 = A dx$). Since the acceleration of the piston is not zero, this energy is not longer in general equal to $(P_1 - P_2)dV_1$.

The internal energy of each side evolves in the following way

$$dU_1 = \begin{cases} \chi \kappa v dx - P_1 dV_1 & \text{if } 0 \leq v \\ (1 - \chi) \kappa v dx - P_1 dV_1 & \text{if } v < 0 \end{cases}$$

$$\text{Eq 15}$$

$$dU_2 = \begin{cases} (1 - \chi) \kappa v dx + P_2 dV_1 & \text{if } 0 \leq v \\ \chi \kappa v dx + P_2 dV_1 & \text{if } v < 0 \end{cases}$$

where $\chi$ is the fraction of the energy $\kappa v dx$ gained by the expanding side. This set of three equations (Equations 14 and 15) could only be solved numerically even if $\chi$ is assumed to be constant.

A more precise functional dependence of $\chi$ could be calculated from kinetic theory for a particular system. It is also possible to treat $\chi$ as a parameter for fitting experimental data.

VIII. Conclusions

The Entropy Maximum Principle was applied to a system consisting of a gas-containing box divided by a piston. The determination of the equilibrium conditions employing this principle has been a long open-problem of thermodynamics. The discrepancies arise from a generalized error in the mathematical approaches consisting of not guaranteeing that the energy remains constant when the piston moves. The energy can only stay constant if the energy lost in the form
of work is returned in the system in the form of internal energy. This is, in fact, the natural way in which the entropy increases. When the energy is actually kept constant, the equilibrium conditions follow naturally. An important conclusion is that the equality of the pressures of both sides when the piston is allowed to move is an equilibrium condition directly obtained from the Entropy Maximum Principle. The equality of the chemical potentials when particles could be interchanged is also a natural consequence of the Entropy Maximum Principle.

When the system is isolated and the Entropy Maximum Principle is applied, part of the energy returned to the system is incorporated into one of the two sides and the rest into the other. This is quantified by the introduction of the parameter $\chi$. The approach proposed in this paper provides a means to solve particular problems in terms of this parameter. For cases in which $\chi$ could be considered constant all along the way to the equilibrium state, it is possible to find analytical solutions for simple gases. For numerical analysis of experimental data, $\chi$ could be treated as a fitting parameter. More precise determinations of $\chi$ could involve the application of kinetic theory. The introduction of this parameter clearly illustrates that the final state depends on the details of the process and of the system. It also illustrates that those details could be in principle quantified through a proper model for $\chi$. The calculation of the evolution of systems exchanging volume and/or particles should include a treatment of the parameter $\chi$.

Although not widely recognized, another long standing problem of thermodynamics is the extraction of the equilibrium conditions form the Energy Minimum Principle. A common error is trying to apply the principle without assuring that the entropy remains constant during the quasistatic process. If the constancy of the entropy is guaranteed in the calculations (by means of extracting heat from the system), it is possible to show, without circular arguments, that thermodynamic equilibrium requires that the temperatures are equal in both sides when heat flow is allowed. When the Energy Minimum Principle is applied and the total entropy is guaranteed to be constant, part of the heat that has to be extracted comes from one side and the rest from the other. This is quantified by the introduction of the parameter $\zeta$. In the same way, its introduction is important for didactical purposes since it illustrates that the final state depends on the details of the system (quantified through $\zeta$).

The equality of the temperatures, pressures, and chemical potentials when heat can flow, volume can change, and particles can permeate, respectively, is naturally reached regardless the total internal energy is kept constant (employing the Entropy Maximum Principle) or the total entropy is kept constant (employing the Energy Minimum Principle).

The statements of the Entropy Maximum Principle and of the Energy Minimum Principle should not be done in terms of the internal parameters but instead in term of internal variations or changes.

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