On the problem of thermodynamic equilibrium in the presence of internal adiabatic constraints

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Abstract. An isolated system consisting of an ideal gas separated into two parts by an adiabatic piston, initially subjected to different pressures, is considered. This is well known as a system with incomplete information from a purely thermodynamic viewpoint, in so far as the final equilibrium state is concerned. However, at least for an ideal gas, the fact that the final equilibrium pressure depends only on the total energy and volume of the system, in conjunction with an *ad hoc* conjecture advanced by the authors, allows one to completely remove the indeterminacy of the problem. Indeed, it is shown that the proposed new relation, which asserts that the equilibrium pressure is equal to a suitably defined mean pressure acting on the piston, allows one to find a unique solution while remaining entirely within a thermodynamic framework. It is also shown that, among all possible functional relations, the equality of these two pressures is the only one always consistent with the second law of thermodynamics. The results derived, however, are strictly valid only for ideal gases.

1. Introduction

In appendix C of his excellent text on thermodynamics [1]†, Callen faces the problem of thermodynamic equilibrium for gaseous systems having internal adiabatic constraints. He deals with the following case as an example.

A gas is contained in a cylinder having rigid, adiabatic walls, which are also impermeable to any substance. The cylinder is divided into two parts, A and B, by a moveable piston, which is adiabatic and impermeable to any substance as well. If the constraints which initially keep the piston steady are removed, the piston will start moving in the direction of least pressure and then carry out a series of damped oscillations. For the sake of simplicity, let us neglect the friction between the piston and the walls of the cylinder. Nevertheless, the internal fluid viscosity alone is able to progressively damp out the oscillations of the piston. Thus, the system can reach a final state of equilibrium in which, of course, the pressure is the same for both subsystems A and B. As for the temperature, it need not be the same for both subsystems in equilibrium. The point is, as Callen clearly states, that these two equilibrium temperatures cannot be determined unless further information is given about kinetic parameters (for example, the gas viscosity) which cannot be included in a purely thermodynamic treatment. In Callen's assessment, since in cases like this the maximum entropy principle is inadequate, only three relations are available, namely,

$$U_A + U_B = U \tag{1.1}$$
$$V_A + V_B = V \tag{1.2}$$
$$p_A = p_B \tag{1.3}$$

† See, equivalently, problem 2.7-3 in [2].

where U_A, V_A and p_A are, respectively, the internal energy, the volume and the pressure of gas A at the equilibrium; U_B, V_B and p_B are the analogous quantities for gas B; while U and V are the constant internal energy and the constant volume of the whole, two-gas system.

If the equation of state of the gas is known, p_A and p_B can be expressed as functions of the respective extensive variables:

$$p_A = p(U_A, V_A) \qquad p_B = p(U_B, V_B). \tag{1.4}$$

Thus, relations (1.1)–(1.3) constitute a system of three equations in the four unknowns U_A, V_A, U_B, V_B, the solution of which cannot be determined unless another relation between at least two of these unknowns is available. Searching for a missing relation within a purely thermodynamic framework is the purpose of this work.

2. Preliminary computations

We will examine only the case of gases which are sufficiently rarefied that they may be regarded as ideal, and whose heat capacities may be assumed to be constant (i.e. independent of temperature). The reason is that ideal gases enjoy a particular property which is essential for our solution of the problem.

Indeed, if T_A and T_B denote the equilibrium temperatures of the gases, n_A and n_B the respective numbers of moles, and C_V the common heat capacity at constant volume, the internal energies are simply $U_A = n_A C_V T_A$ and $U_B = n_B C_V T_B$. As a consequence, the equations of state of the two gases can be rewritten as

$$p_A = \frac{R}{C_V} \frac{U_A}{V_A} \qquad p_B = \frac{R}{C_V} \frac{U_B}{V_B} \tag{2.1}$$

where R is the universal gas constant. Therefore, equation (1.3) yields

$$\frac{U_A}{V_A} = \frac{U_B}{V_B}. \tag{2.2}$$

On eliminating U_B and V_B among the latter equation and equations (1.1) and (1.2), one obtains

$$\frac{U_A}{V_A} = \frac{U}{V}. \tag{2.3}$$

Of course, an analogous relation holds for gas B, so that, on denoting by p_E the common pressure at equilibrium, each of equations (2.1) becomes

$$p_E = \frac{R}{C_V} \frac{U}{V}. \tag{2.4}$$

Thus, the system of the two gases enjoys the property that its equilibrium pressure can be determined even though the number of relations available is one less than the number of relevant unknowns characterizing its final equilibrium. In fact, p_E depends only on the total energy and volume of the system, or, in other words, is independent of how U and V are initially distributed between the two gases.

Note also that, if $U_{A,0}$, $V_{A,0}$ and $p_{A,0}$ are, respectively, the internal energy, the volume, and the pressure of gas A at the beginning of the process, and $U_{B,0}$, $V_{B,0}$ and $p_{B,0}$ are the analogous quantities for gas B, then one has

$$U_{A,0} + U_{B,0} = U \qquad V_{A,0} + V_{B,0} = V \tag{2.5}$$

and

$$p_{A,0} = \frac{R}{C_V} \frac{U_{A,0}}{V_{A,0}} \qquad p_{B,0} = \frac{R}{C_V} \frac{U_{B,0}}{V_{B,0}}. \tag{2.6}$$

Hence equation (2.4) becomes

$$p_E = \frac{p_{A,0} V_{A,0} + p_{B,0} V_{B,0}}{V_{A,0} + V_{B,0}} \tag{2.7}$$

or, equivalently,

$$p_E = \frac{U_{A,0} + U_{B,0}}{(U_{A,0}/p_{A,0}) + (U_{B,0}/p_{B,0})}. \tag{2.8}$$

Both equations (2.7) and (2.8), being weighted averages, show that, as one might suppose, the final equilibrium pressure p_E is intermediate between $p_{A,0}$ and $p_{B,0}$ and in particular, that if these initial pressures happen to be equal, then the equilibrium pressure has this same value.

3. Lower and upper bounds to the equilibrium values

In searching for a missing relation (that should link energy and volume of either gas in its final state), since no use has been made so far of the second law of thermodynamics, it is quite natural to wonder what sort of information might be drawn from it.

Since both gases undergo an irreversible process with no heat exchange, the entropy of neither of them can decrease. More precisely, one can write the molar entropy change of, say, gas A, as $\Delta s_A = \Delta s_A^{(r)} + \Delta s_A^{(g)}$ where the entropy received, $\Delta s^{(r)}$, must vanish for an adiabatic process, while the internally generated entropy, $\Delta s^{(g)}$, cannot be negative. Hence, using the expression for the entropy of ideal gases with constant C_V yields

$$\Delta s_A = C_V \ln\left(\frac{U_A}{U_{A,0}}\right) + R \ln\left(\frac{V_A}{V_{A,0}}\right) \geqslant 0. \tag{3.1}$$

Now, on making use of equations (2.3) and (2.6), one can eliminate $V_A/V_{A,0}$ so that, having regard to equation (2.4), this inequality becomes

$$\frac{U_A}{U_{A,0}} \geqslant \left(\frac{p_E}{p_{A,0}}\right)^{R/C_p} \tag{3.2}$$

where $C_p = C_V + R$ is the molar heat capacity of the ideal gas at constant pressure. Similarly, for gas B one has

$$\frac{U_B}{U_{B,0}} \geqslant \left(\frac{p_E}{p_{B,0}}\right)^{R/C_p} \tag{3.3}$$

or

$$\frac{U - U_A}{U_{B,0}} \geqslant \left(\frac{p_E}{p_{B,0}}\right)^{R/C_p}. \tag{3.4}$$

Thus, combining (3.2) and (3.4), the condition

$$\frac{U_{A,0}}{U}\left(\frac{p_E}{p_{A,0}}\right)^{R/C_p} \leqslant \frac{U_A}{U} \leqslant 1 - \frac{U_{B,0}}{U}\left(\frac{p_E}{p_{B,0}}\right)^{R/C_p} \tag{3.5}$$

must be satisfied at any equilibrium. As for the volume, an analogous procedure leads to

$$\frac{V_{A,0}}{V}\left(\frac{p_{A,0}}{p_E}\right)^{C_V/C_p} \leqslant \frac{V_A}{V} \leqslant 1 - \frac{V_{B,0}}{V}\left(\frac{p_{B,0}}{p_E}\right)^{C_V/C_p}. \tag{3.6}$$

Of course, similar bounds hold for gas B. Note that the bounds in (3.5) must coincide with those in (3.6), since V_A/V always coincides with U_A/U in view of equation (2.3). In general let

$$\alpha \equiv \frac{U_{A,0}}{U_{B,0}} \qquad \beta \equiv \frac{V_{A,0}}{V_{B,0}} \tag{3.7}$$

whence $p_{A,0}/p_{B,0} = \alpha/\beta$. Then, in the initial state one has, in terms of the dimensionless independent parameters α and β,

$$\frac{U_{A,0}}{U} = \left(1 + \frac{1}{\alpha}\right)^{-1} \qquad \frac{U_{B,0}}{U} = (1 + \alpha)^{-1} \tag{3.8}$$

$$\frac{V_{A,0}}{V} = \left(1 + \frac{1}{\beta}\right)^{-1} \qquad \frac{V_{B,0}}{V} = (1 + \beta)^{-1} \tag{3.9}$$

$$\frac{p_E}{p_{A,0}} = \left(1 + \frac{1}{\alpha}\right)\left(1 + \frac{1}{\beta}\right)^{-1} \qquad \frac{p_E}{p_{B,0}} = (1 + \alpha)(1 + \beta)^{-1}. \tag{3.10}$$

Thus, equations (3.5) and (3.6) become

$$\left(1 + \frac{1}{\alpha}\right)^{-C_V/C_p} \left(1 + \frac{1}{\beta}\right)^{-R/C_p} \leqslant \frac{U_A}{U} \leqslant 1 - (1 + \alpha)^{-C_V/C_p}(1 + \beta)^{R/C_p} \tag{3.11}$$

and

$$\left(1 + \frac{1}{\alpha}\right)^{-C_V/C_p} \left(1 + \frac{1}{\beta}\right)^{-R/C_p} \leqslant \frac{V_A}{V} \leqslant 1 - (1 + \alpha)^{-C_V/C_p}(1 + \beta)^{R/C_p}. \tag{3.12}$$

As noted above, the bounds appearing in (3.11) coincide with those in (3.12).

Supposing our gas to be monatomic so that $C_p = 5R/2$ and $C_V = 3R/2$, let us calculate, as an example, the equilibrium values of energy and volume for $p_{A,0} = 2p_{B,0}$ and $V_{A,0} = V_{B,0}$, namely for $\alpha = 2$ and $\beta = 1$. In this case (3.11) yields for gas A

$$0.594 \leqslant \frac{U_A}{U} \leqslant 0.608$$

and for gas B

$$0.392 \leqslant \frac{U_B}{U} \leqslant 0.406$$

each ratio being the complement to unity of the other. The bounds for the volumes are the same as for the energy, as noted above. In conclusion, the second law dictates definite bounds for the equilibrium values of energy and volume, but, however close the bounds may be, the solution of the problem still remains undetermined.

4. A spontaneous adiabatic process

Before continuing the analysis of the problem raised by Callen, it is instructive to examine a simpler case of an adiabatic process, since, by analogy, it might point the way to a unique solution of Callen's problem from a purely thermodynamic viewpoint.

Accordingly, consider a gas contained in a cylinder with rigid, impermeable and adiabatic walls. One of the bases of the cylinder is fixed while the other is a moveable piston, through which the system can exchange only work with a reservoir maintained at a fixed pressure p_E. Let the initial internal pressure of the gas be p_0. If the constraints which initially keep the piston steady are removed, the piston will start to move inwards

or outwards depending on whether the gas pressure is lower or higher than the reservoir's. Then the piston will carry out a series of damped oscillations before stopping in a position of equilibrium, that, as shown below, can be uniquely determined by the first law of thermodynamics and the equation of state. What we want to point out now is that the final equilibrium pressure of the gas turns out to coincide with a suitably defined average of the mechanical pressure exerted by the gas on the piston during the process of expansion or contraction.

First, it must be recognized that during the process the pressure inside the gas has to be regarded in general as a function of space and time. However, the mechanical pressure p_m over the piston surface may be assumed to be uniform, although variable in time. Thus, if the piston carries out N oscillations before stopping, the work done by the gas on the piston may be written as

$$L = \sum_{i=1}^{N} \int_{V_{i-1}}^{V_i} p_m \, \mathrm{d}V \tag{4.1}$$

where V_0 is the initial volume of the gas and $V_1, V_2, \ldots, V_N \equiv V_E$ are the volumes at the end of the first, the second, ..., the Nth oscillation. If we now introduce the quantity

$$\bar{p} = \frac{1}{V_E - V_0} \sum_{i=1}^{N} \int_{V_{i-1}}^{V_i} p_m \, \mathrm{d}V \tag{4.2}$$

which may be called the mean pressure on the piston, then

$$L = \bar{p}(V_E - V_0). \tag{4.3}$$

Let us now focus attention on the piston. Since it is at rest both at the beginning and at the end of the process, even if it eventually stops at a different position, the general work-energy theorem of mechanics ensures that the total work done by all the forces acting upon it is zero. Since we have assumed no friction between the piston and the walls of the cylinder, it can be concluded that the work L done by the gas on the piston, given by (4.3), is exactly opposite to the work

$$L_{\text{ext}} = -p_E(V_E - V_0) \tag{4.4}$$

done upon it from outside. Hence one has

$$\bar{p} = p_E \tag{4.5}$$

that is, the mean pressure on the piston coincides with the reservoir's pressure, which, of course, is the final equilibrium pressure. This result, although simple, can be of some importance. Indeed, as noted above, were it possible to somehow extrapolate it to the case dealt with by Callen, it would then provide the one missing relation necessary to find a unique solution for that problem.

In any case, since the process being considered takes place with no heat exchange, the variation in internal energy is, in the light of (4.4)

$$U_E - U_0 = -p_E(V_E - V_0). \tag{4.6}$$

If the equation of state of the gas is known, p_E can be expressed as a function of U_E and V_E, or

$$p_E = p(U_E, V_E). \tag{4.7}$$

The previous two equations constitute a system in two unknowns, U_E and V_E, the solution of which yields the final state of equilibrium. For an ideal gas with constant heat capacities equation (4.7) takes the simple form

$$p_E = \frac{R}{C_V} \frac{U_E}{V_E} \tag{4.8}$$

and the solution, as easily verified, is given by

$$\frac{U_E}{U_0} = \frac{C_V}{C_p} + \frac{R}{C_p} \frac{p_E}{p_0} \qquad \frac{V_E}{V_0} = \frac{R}{C_p} + \frac{C_V}{C_p} \frac{p_0}{p_E}. \tag{4.9}$$

5. A purely thermodynamic treatment of Callen's problem

Let us now return to the problem discussed by Callen. If $\bar{p}_A$ and $\bar{p}_B$ denote the mean pressures of gas A and gas B on the piston, defined according to (4.2), then the work done by the forces exerted by each gas on the piston is, in analogy with equation (4.3),

$$L_A = \bar{p}_A(V_A - V_{A,0}) \qquad L_B = \bar{p}_B(V_B - V_{B,0}). \tag{5.1}$$

On the other hand, since there is no heat exchange, one must have

$$U_A - U_{A,0} = -L_A \qquad U_B - U_{B,0} = -L_B \tag{5.2}$$

whence $L_A + L_B = 0$, the total energy being constant. Then from (5.1) one has $\bar{p}_A = \bar{p}_B$, the total volume also being constant. Thus, on denoting by $\bar{p}$ the common value of the mean pressures on the piston, the first of the two relations (5.1) becomes

$$L_A = \bar{p}(V_A - V_{A,0}) \tag{5.3}$$

whence

$$U_A - U_{A,0} = -\bar{p}(V_A - V_{A,0}). \tag{5.4}$$

A similar relation holds for gas B, but in virtue of the conservation rules (1.1) and (1.2), it is nothing but a consequence of equation (5.4). Thus, equations (1.1)–(1.3) and (5.4) constitute a system of four equations in the five unknowns U_A, V_A, U_B, V_B and $\bar{p}$. After eliminating U_B and V_B this system reduces to the system of equations (2.3) and (5.4) in the three unknowns U_A, V_A and $\bar{p}$, so the problem still remains indeterminate.

In any case, if equation (2.3) is written, according to (2.4), as

$$\frac{U_A}{V_A} = \frac{C_V}{R} p_E \tag{5.5}$$

after eliminating V_A between this equation and equation (5.4), and recalling (2.6), one obtains

$$\frac{U_A}{U_{A,0}} = \frac{1 + \frac{R}{C_V} \frac{\bar{p}}{p_{A,0}}}{1 + \frac{R}{C_V} \frac{\bar{p}}{p_E}}. \tag{5.6}$$

Similarly, after eliminating U_A between (5.4) and (5.5), one has

$$\frac{V_A}{V_{A,0}} = \frac{1 + \frac{C_V}{R} \frac{p_{A,0}}{\bar{p}}}{1 + \frac{C_V}{R} \frac{p_E}{\bar{p}}}. \tag{5.7}$$

Of course, similar relations hold for gas B.

Note that, whatever $\bar{p}$ may be, from (5.6) and (5.7) it is evident, since the value of p_E is intermediate between the initial pressures, that the gas initially at lower pressure gets

compressed and heats up, whereas the other expands and cools down. In particular, if there is no difference in the initial pressures, no change at all can occur after releasing the piston.

Of course, these same results could be derived as a consequence of the second law, for example via equation (3.2).

6. A proposed relation for solving the problem

It is quite natural to wonder whether a thermodynamic relation exists linking the mean pressure on the piston $\bar{p}$ to the equilibrium gas pressure p_E. The strong analogy between the problem dealt with by Callen and that discussed in section 4 suggests that one may simply assume

$$\bar{p} = p_E \tag{6.1}$$

in analogy to equation (4.5). If this equality held, equations (5.6) and (5.7) would reduce exactly to equations (4.9) for the one-gas system, that is

$$\frac{U_A}{U_{A,0}} = \frac{C_V}{C_p} + \frac{R}{C_p} \frac{p_E}{p_{A,0}} \qquad \frac{V_A}{V_{A,0}} = \frac{R}{C_p} + \frac{C_V}{C_p} \frac{p_{A,0}}{p_E}. \tag{6.2}$$

These relations, together with their analogues for gas B, would then represent the unique solution of the problem. For example, in the case of a monatomic gas with $\alpha = 2$, $\beta = 1$, as treated in section 3, one would get

$$U_A = \tfrac{9}{10} U_{A,0} \qquad V_A = \tfrac{6}{5} V_{A,0}$$

and

$$U_B = \tfrac{6}{5} U_{B,0} \qquad V_B = \tfrac{4}{5} V_{B,0}.$$

The total energy U in the final state of equilibrium would be distributed as

$$U_A = \tfrac{3}{5} U \qquad U_B = \tfrac{2}{5} U.$$

Equation (2.3) implies that the same distribution would hold for the total volume of the system.

The above values for the ratios U_A/U and U_B/U fall within the narrow ranges—respectively $(0.594, 0.608)$ for gas A and $(0.392, 0.405)$ for gas B—derived at the end of section 3. In other words, in this case the proposed equality (6.1) is not inconsistent with the second law. As a matter of fact, it can be shown easily that in no case (namely, whatever the initial state of the two-gas system) does the proposed equality engender a contradiction with fundamental principles. Indeed, on making use of the two relations (6.2), the entropy change (3.1) of either gas, say gas A, can be expressed as

$$\Delta s_A = C_V \ln \left(\frac{C_V}{C_p} + \frac{R}{C_p} \frac{p_E}{p_{A,0}} \right) + R \ln \left(\frac{R}{C_p} + \frac{C_V}{C_p} \frac{p_{A,0}}{p_E} \right). \tag{6.3}$$

By simply scrutinizing $\Delta s_A/R$ as a function of the variable $x \equiv p_{A,0}/p_E$ (see curve (a) in figure 1), one concludes that it is continuous and monotonically decreasing for $p_E < p_{A,0}$ but monotonically increasing for $p_E > p_{A,0}$. Since $\Delta s_A = 0$ for $p_E = p_{A,0}$, it follows that the entropy change (6.3) is never negative, in agreement with the second law. Obviously, this result also holds for gas B.
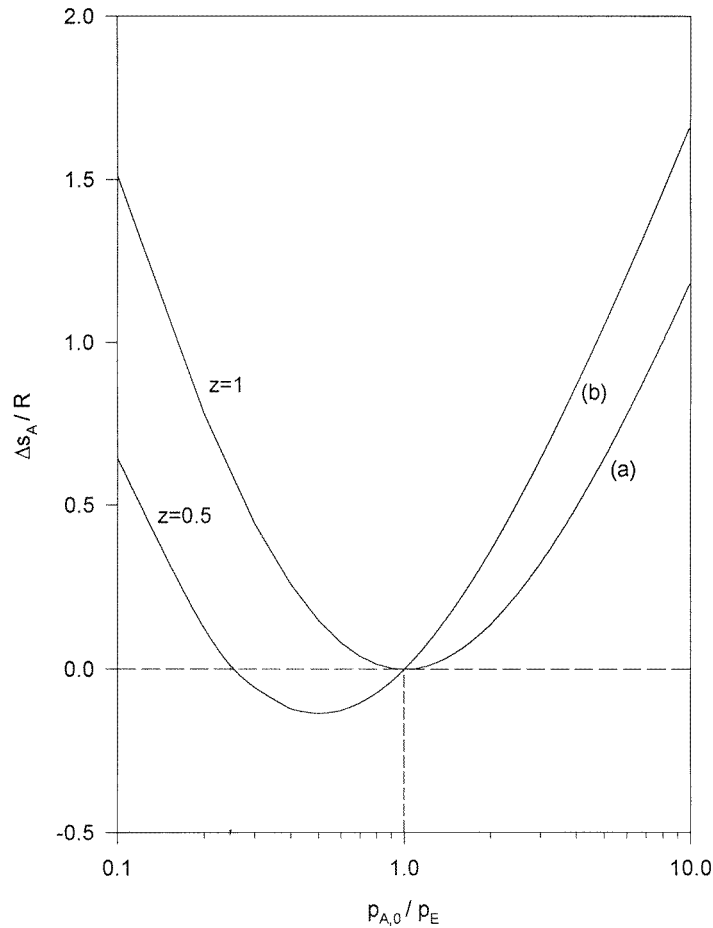
Figure 1. Dimensionless molar entropy change of either of the two gases as a function of the ratio of initial to final pressure, under the assumptions that the mean pressure on the piston is equal to (a) the final equilibrium pressure, (b) half that value. In case (a) the entropy change is never negative, for any initial conditions, in agreement with the second law, whereas in case (b) it proves to be negative in an interval of initial conditions ranging from $p_{A,0} = 0.26p_E$ to $p_{A,0} = p_E$, thereby violating the second law.

7. Concluding remarks

The fact that the assumption (6.1) is never in conflict with the second law is a necessary but not sufficient condition for its validity. Thus, it is quite natural to wonder whether any other law relating $\bar{p}$ to p_E can exist which remains consistent with the second law for all possible states in which the two-gas system might start. It can be shown that no such alternative relation exists.

Indeed, consider any law relating $\bar{p}$ to p_E different from equation (6.1). Then there will exist at least one value of p_E such that $\bar{p}$ does not coincide with p_E. In this case, on inserting equations (5.6) and (5.7) into (3.1), the molar entropy change of either gas, say

gas A, may be expressed as

$$\frac{\Delta s_A}{R} = \lambda \ln \left(\frac{1 + z/\lambda x_A}{1 + z/\lambda} \right) + \ln \left(\frac{1 + \lambda x_A/z}{1 + \lambda/z} \right) \tag{7.1}$$

where

$$\lambda = C_V/R \qquad z = \frac{\bar{p}}{p_E} \qquad x_A = \frac{p_{A,0}}{p_E}. \tag{7.2}$$

When written in this form, Δs_A may be regarded, for a given value of z, as a function of x_A, or, since p_E is fixed, as a function of $p_{A,0}$. As an example, curve (b) in figure 1 shows, for $z = 0.5$, the behaviour of $\Delta s_A/R$ for a monatomic ideal gas when x_A is varied. It is seen that the entropy change is negative in the interval $(0.26, 1)$. This means that, whenever $p_{A,0}$ is chosen so that x_A belongs to this interval—as can always be done physically—the value $z = 0.5$ would lead to a violation of the second law.

It is straightforward to verify that the same situation arises whenever $z \neq 1$. In other words, for any value of $\bar{p}$ different from p_E there will exist a definite set of initial states for which the second law is violated (see appendix). Obviously, the same argument applies if one makes the assumption that $\bar{p}$, like p_E, also depends only on the total energy and the total volume, but in a manner different from p_E.

It can therefore be concluded that, if there is a law directly linking p_E and $\bar{p}$ it must be $\bar{p} = p_E$, while the only alternative to this identity is that $\bar{p}$ necessarily depends on how the total volume and total energy of the two-gas system are initially distributed between the two components A and B.

Finally, it should be noted that the assumption (6.1) can also be regarded as a strong constraint imposed upon the possible dynamical paths leading the two-gas system to final thermodynamic equilibrium. Indeed, the relation (6.1) implicitly states that the mean mechanical pressure on the piston during the spontaneous process has a definite functional dependence upon the total energy and volume of the system, no matter how U and V are distributed between the two gases. Or, to be more precise, it is prescribed that the mean pressure $\bar{p}$ depends on U and V in exactly the same way as does p_E, namely, according to equation (2.4).

In conclusion, it can be stated that the information added by the proposal (6.1) removes the indeterminacy of Callen's problem, as far as ideal gases are concerned, and allows one to find a unique solution, represented by (6.2), while still remaining within an entirely thermodynamic framework.

Note that for nonideal gases no immediate generalization of the present treatment is possible. In fact, in contrast to an ideal gas which satisfies equation (2.4), the equilibrium pressure cannot be predicted given only the equation of state. Its determination requires, in general, some further information about the system. Thus, all the results derived here are strictly valid only for ideal gases.

Appendix

In our notation it is clear that, once given the total energy U and the total volume V, assigning an initial state of the two-gas system is equivalent to assigning the values of x_A and x_B, one of which lies in the interval $[0, 1]$ while the other exceeds unity. Suppose now, with no loss of generality, that gas A is the one starting with lower pressure so that $x_A < 1$ and $x_B > 1$. Since the molar entropy change Δs_A must be non-negative, a trivial

manipulation of (7.1) yields

$$\left(\frac{\lambda + z/x_A}{\lambda + z}\right)^\lambda \left(\frac{\lambda x_A + z}{\lambda + z}\right) \geqslant 1. \tag{A.1}$$

Hence, since x_A is positive, one immediately finds

$$\frac{\lambda x_A + z}{\lambda + z} \geqslant x_A^v \tag{A.2}$$

where we have used $v \equiv \lambda/(1 + \lambda) = C_V/C_p$. The solution of this simple inequality in z, recalling that x_A is also less than unity, is

$$z \geqslant \frac{v}{1 - v} \frac{x_A^v - x_A}{1 - x_A^v}. \tag{A.3}$$

Starting now with the analogue of (7.1) for gas B, a similar derivation leads on the other hand to

$$z \leqslant \frac{v}{1 - v} \frac{x_B^v - x_B}{1 - x_B^v}. \tag{A.4}$$

Obviously, the roles of gases A and B would be reversed if the latter started with the lower pressure. In any case, it can be stated that the bounds for z ensuring no violation of the second law are obtained by evaluating the function

$$f(x) \equiv \frac{v}{1 - v} \frac{x^v - x}{1 - x^v} \tag{A.5}$$

at $x = x_A$ and $x = x_B$, the lower function value yielding the lower bound for z.

For example, for $\alpha = 2$ and $\beta = 1$ (see section 3) one has $x_A = \frac{4}{3}$ and $x_B = \frac{2}{3}$, and for a monatomic ideal gas ($v = \frac{3}{5}$) the latter equation yields $f(x_A) = 1.15$ and $f(x_B) = 0.815$. Therefore, in this case the ratio $\bar{p}/p_E$ must belong to the interval $(0.815, 1.15)$.

In general, the function (A.5), after defining $f(1) \equiv 1$, is a continuous function for any $x \geqslant 0$ monotonically increasing from zero to infinity, so that $x < 1$ implies $f(x) < 1$ while $x > 1$ implies $f(x) > 1$. Hence, for any choice of the initial state of the two-gas system, the physically permitted range for the quantity $z \equiv \bar{p}/p_E$ is always a neighbourhood of unity and the only point common to all such intervals is the point $z = 1$. Therefore it can be concluded that $\bar{p} = p_E$ is the unique relation—provided there is such a relation linking the two pressures—that ensures that the second law holds whatever the initial state of the two-gas system.

References

[1] Callen H B 1960 *Thermodynamics* (New York: Wiley)
[2] Callen H B 1985 *Thermodynamics* 2nd edn (New York: Wiley)