RESOLUTION OF TWO ENTROPY MAXIMIZATION CONTROVERSIES

Rodrigo de Abreu
Departamento de Física e Centro de Electrodinâmica,
Instituto Superior Técnico, Lisboa.

Consideration of the irreversible processes resulting from the interaction between two subsystems (consisting of ideal gases) resulted in two controversies [1-16]. The resolution of these controversies can be achieved by analyzing relevant contradictory formulations [2-4, 5, 8-11, 12, 15, 16]. Comments on one of this controversies were published recently in the JCE [16] and were about an earlier article published in the JCE [15].

The analysis of several processes involving the interaction between two ideal gases clears up the physical meaning of the equations and permits the determination of the final equilibrium state. If one of the subsystems is at constant volume, the increase of the entropy of the universe, the global entropy increase, the Second Law, implies the local law, the positive entropy production. If the volumes of the subsystems change through the movement of a partition, it is not possible to generalize the equations for this configuration. The local law for the first case (the volume is constant) it is unnecessary, for the other it doesn't make sense. For one case it gives a false interpretation [15-16]. For the other it was the source of a false impossibility statement [1-14]. To show that we need to consider two configurations:

1. One mole of an ideal gas A occupies an initial volume V_{Ai} and the initial temperature is T_{Ai} . One mole of an ideal gas B occupies an initial volume V_{Bi} and the initial

temperature is T_{Bi}. For this first configuration the gas A is connected with gas B and the volume of gas B is constant. Energy flows from A to B, because $T_{Bi}<T_{Ai}$. The final temperature, we impose, is $T_{Af} =T_{Bf}=T_{Ai}$, since work is done by an exterior force. The work is equal to the potential energy change of a part of the universe, without entropy change [17, 18]. This configuration originates, recently, a controversy [15-16].

2. One mole of an ideal gas occupies an initial volume V_{Ai} and the initial temperature is T_{Ai} . The interaction between the two gases results from the movement of a piston, that separates the two gases. The total volume is constant, $V=V_A+V_B$. The initial temperature of B, T_{Bi} is lower than the temperature of A, $T_{Ai..}$. This configuration also gives a controversy [1-14].

I. The Fundamental Relation of Thermodynamics dU=-pdV+TdS, the First and Second Laws of Thermodynamics - meaning and validity conditions.

Internal energy U , entropy S, volume V, pressure p and temperature T are related by the following expressions

$$U = U(V,S) \qquad (1)$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad (2)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p. \qquad (3)$$

Since

$$dU = < \mathbf{d}U, dP > \qquad (4)$$

with $\mathbf{d}U = \left(\frac{\partial U}{\partial V}\right)_S \mathbf{d}V + \left(\frac{\partial U}{\partial S}\right)_V \mathbf{d}S$ (**d** is the exterior differential) and (4) is the contraction of form **d**U with vector **dP**=dV $\mathbf{u}_V$ +dS $\mathbf{u}_S$ [19], we have

$$dU = -pdV + TdS\,. \qquad (5)$$

Lets us consider a process described in time by U=U(t), V=V(t) . Since U=U(V,S), exists one S(t) satisfying U(t)=U[V(t),S(t)]. If we put the subsystem at an equilibrium point with energy U=U(t), volume V=V(t) and entropy S=S(t) then makes sense the quantities

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

and

$$T = \left(\frac{\partial U}{\partial S}\right)_V,$$

p and T are the pressure and the temperature at the equilibrium point with energy U=U(t) the same volume V(t) and the same entropy S(t) . It is important to remark that when the subsystem describes in time an actual trajectory, does not make sense the temperature and the pressure for the actual trajectory. But the meaning is clear for the equilibrium points with the same energy, the same entropy and the same volume. Lets call this points equivalent equilibrium points (EP). Since dU=-pdV+TdS from (4), equation (5) is general and well defined for any process.

A reversible process is a process which can be globally reverted. This process is obviously isentropic. As an example lets consider the reversible adiabatic compression of an ideal gas. From the energy conservation law and from equation (5) we have

$$dW_{ext} = dU, \qquad (6)$$

$$dW_{ext} = -p_{ext}dV, \qquad (7)$$

$$-p_{ext}dV = -pdV + TdS\ , \qquad (8)$$

$$p_{ext} = p \quad , \qquad (9)$$

$$dS = 0\,, \qquad (10)$$

and if compressed isothermally and reversibly we have

$$dW_{ext} = dU + dU_H, \qquad (11)$$

where dW_{ext} is the work of an exterior force and dU_H the variation of the internal energy of a heat source. From (5), (7) and (11) we have

$$-p_{ext}dV = -pdV + TdS + TdS_H, \qquad (12)$$

$$p_{ext} = p, \qquad (13)$$

$$dS + dS_H = 0\,. \qquad (14)$$

To be reversible it was necessary that the exterior pressure was equal to the interior pressure, and evidently, the initial state was a global equilibrium point with the same temperature T for all the subsystems.

It is also important to remark, for a compression or expansion, the piston which permits the change of volume has mass. The piston kinetic energy E_{kin} satisfies the following relation

$$dW = dE_{kin}, \qquad (15)$$

with $$dW = dW_{ext.} + dW_{int.} = -p_{ext} dV + p' dV \quad . \qquad (16)$$

dW_{int} is the work done by an interior pressure p' , the dynamic pressure over the piston, which is different from the equilibrium pressure p. If the piston speed is not zero, for a compression the dynamic pressure is higher than the equilibrium pressure and for an expansion the dynamic pressure is smaller than the equilibrium pressure (for a reversible process those pressures are equal because the piston speed is zero) [20].

For an irreversible process the energy conservation principle must consider the kinetic energy change of the piston (dE_{kin})

$$dE_{kin} + dE_{pot} + dU = 0 \; , \qquad (17)$$

and

$$dW_{ext} = -dE_{pot} \, , \qquad (18)$$

therefore from (15), (17) and (18)

$$-d(E_{kin}+E_{pot}) = dU = -dW + dW_{ext} = -dW_{int} = -p'dV. \qquad (19)$$

Then, for an irreversible process,

$$-d(E_{kin}+E_{pot}) = -dW_{int} = dU = -p'dV \qquad (20)$$

and from (5)

$$-dW_{int} = -p'dV = dU = -pdV + TdS. \qquad (21)$$

If the process was reversible

$$-dW_{int} = dW_{ext} = dU. \qquad (22)$$

If the System contains a heat source with energy U_H and not only U, then we have

$$dW_{int} = -p'dV = dU + dU_H = -pdV + TdS + T_H dS_H. \qquad (23)$$

The Second Law states that the change of entropy of a System (whole subsystems) is equal or greater than zero. When p=p' and $T=T_H$, $dS+dS_H=0$. If dV<0 , p'≥p. If dV>0, p'≤p. For both cases, since T and T_H are greater then zero, and since the energy flows from the higher temperature subsystem to the one with lower temperature,$dS+dS_H>0$. The positive entropy variation results from the energy exchanges and from the change of volume due to the interaction with the piston, and the energy exchange between the subsystems at different temperatures. When the interaction between the subsystems is achieved by the movement of a movable partition separating the two gases, relations (21) and (22) are verified with $U=U_A+U_B$ and the dynamic pressure p' is substituted by the difference between the dynamic pressures $p'_A-p'_B$ and TdS is substituted by $T_AdS_A+T_BdS_B$. Although the expression is similar to (23), obviously neither T_AdS_A or T_BdS_B has a similar meaning to the term $T_H\,dS_H$ at expression (23), which can be interpreted as the heat exchanged through the fixed partition. Here the two terms $T_i dS_i$ $(i = A, B)$ has the two effects that change the entropy, the change of volume and the change of energy trough the global movement of the piston. At II, III, IV, V and VI we are going to analyse the interaction between subsystems when the volume of subsystem B is constant, and at VII we are going to consider the interaction when the volume of B changes.

II. Irreversible Isothermal Process (I I P)

Lets consider one mole of an ideal gas A with internal energy $U_A=C_{VA}\,T_A$. Gas B, also ideal, has a constant volume V_B, and the initial temperature is T_{Bi}. If gas A is compressed and if energy can flow from A to B, it is possible, through the compression, to compensate the energy flux to B, and we can have the energy of A constant and therefore the temperature of A constant. The speed of this compression depends of the speed of the energy flow to B. Therefore the exterior pressure is not equal to the interior pressure and the transformation is not reversible, although the temperature that can be associated to A (EP) is constant.

When an equilibrium point is achieved, $T_B = T_{Bf} = T_{Ai}$, we have (integrating (19) between the initial and final states, when the piston is not moving)

$$W_{ext} = \Delta U_A + \Delta U_B \qquad (24)$$

and since $\Delta U_A = 0$

$$W_{ext} = \Delta U_B. \qquad (25)$$

The volume achieved by A, it depends on the value of dW_{ext}, which is determined by the speed of the energy flux to B, conditioned by the geometry of the interaction. Therefore the final equilibrium state, the final volume is not the same for two different apparatus with different geometries.

III. Isothermal "Reversible" Process (I R P)

Another process is the following:

Gas A is compressed reversibly, and the work on this compression $W_{ext} = \Delta U_B$ is introduced in the heat reservoir which is in contact with subsystem A. The temperature of the reservoir is equal to the initial temperature of A, T_{Ai}. After this first process is completed the reservoir transfers to B the same energy that has received ΔU_B. The reservoir returns to the initial state and apparently, but only apparently, did not interfere on the process.

The two previous processes (I I P and I R P) are approximately equivalents. The final volume for A is nearly the same. But rigorously the two processes are not equivalent because the final volume for A is not rigorously the same.

The entropy variation for A is

$$\Delta S_A = R \ln \left(\frac{V_{Af}}{V_{Ai}} \right)$$

and can be calculated by equation (5) through the equivalent points EP, between the initial state and the final state. For the process IRP the final volume is determined by

$$W_{ext} = \int -pdV = \int -R\,T_{Ai}\,\frac{dV_A}{V_A} = C_{VB}\,(T_{Ai} - T_{Bi}). \quad (26)$$

IV. "Isothermal" Irreversible Process with exterior constant pressure.

If gas A was compressed with an exterior constant pressure contacting an heat reservoir at temperature T_{Ai} we have, between the initial and final equilibrium points

$$W_{ext} = -p_{ext}\,\Delta V = \Delta U_H. \quad (27)$$

Lets impose

$$W_{ext} = \Delta U_B = C_{VB}(T_{Ai} - T_{Bi}). \quad (28)$$

When the equilibrium point is attained the temperature of A is evidently T_{Ai} but during the compression, because $p_{ext} \neq p_A$ the temperature is not T_{Ai}.

The final volume can be calculated with (27), (28) and

$$p_{ext}\,V_{Af} = R\,T_{Ai}\,. \quad (29)$$

If the condition of constant temperature was not imposed, although the initial and the final temperature are the same, the final volumes can be very different from the final volume of I R P and consequently from I I P.

If the process was performed contacting directly subsystem B, without the previous contact with a heat reservoir, the final state, the final volume of A, is the same. Equations (28) and (29) determines the same volume for A. The same happens for I R P and I I P when W_{ext} has the same value and the final pressure is the same.

V. The meaning of entropy production.

For the IRP, as was previously verified, the final state can be easily determined and the entropy variation for A is equal to

$$\frac{Q}{T_{Ai}} = \frac{-\Delta U_B}{T_{Ai}}.$$

For the I I P the entropy variation for A, is not equal to

$$\frac{Q}{T_{Ai}} = \frac{-\Delta U_B}{T_{Ai}}. \qquad (30)$$

The entropy production ΔS_{iA} was introduced in the following manner

$$\Delta S_A = \frac{Q}{T_{Ai}} + \Delta S_{iA}. \qquad (31)$$

Equation (31) is verified by definition. Historically entropy was introduced by the relation $dS = \frac{dQ}{T}$ valid on a reversible process. This relation originates a fluid like interpretation, attributing to the expression $dS = \frac{dQ}{T}$ the interpretation that exists an exchange of entropy, not only an exchange of energy. Therefore, if this is so, it was necessary for irreversible processes, to introduce the entropy production term (eq. (31)). The entropy of a subsystem changes either because the energy of the subsystem changes or/and because the deformation variable changes. Those changes for the two quantities, for the System, for a reversible process, compensate each other, and the entropy is constant.

Lets clarify that matter.

For a reversible process, we have:

$$dS + dS_H = 0, \qquad (32)$$

therefore, relation (5) when applied to a heat source, since the volume is constant, gives for (32)

$$dS = -dS_H = -\frac{dU_H}{T} = \frac{dQ}{T}. \qquad (33)$$

For an irreversible process, between two equilibrium points (the piston is also in equilibrium) we have

$$W_{ext} = \int -p_{ext} dV = \Delta U + \Delta U_H. \quad (34)$$

Since $\Delta S_H = \frac{\Delta U_H}{T_H}$ and $\Delta S + \Delta S_H > 0$,

$$\Delta S > -\frac{\Delta U_H}{T_H} \qquad (35)$$

or

$$\Delta S > \frac{Q}{T_H} \qquad (36)$$

since $Q = -\Delta U_H$.

For A interacting with B, similar considerations gives

$$\Delta S_A > \int \frac{dQ}{T_B}. \qquad (37)$$

Since $T_B \leq T_{Ai}$, we have

$$\int \frac{dQ}{T_B} < \frac{Q}{T_{Ai}} \qquad (38)$$

therefore, from (36) and (38)

$$\Delta S_A > \frac{Q}{T_{Ai}} > \int \frac{dQ}{T_B}. \qquad (39)$$

This being so, it is obvious, that we can introduce ΔS_{iA}, satisfying

$$\Delta S_A = \frac{Q}{T_{Ai}} + \Delta S_{iA} \qquad (40)$$

or

$$\Delta S_{iA} = \Delta S_A - \frac{Q}{T_{Ai}}. \qquad (41)$$

Since $\Delta S_A > \dfrac{Q}{T_{Ai}}$,

$$\Delta S_{iA} > 0. \qquad (42)$$

We obtain a positive entropy production from the Second Law. It is not possible to have $\Delta S_{iA} < 0$ [16].

We can obtain the same result from

$$-p'_A dV_A = dU_A + dU_B = -p_A dV_A + T_{Ai} dS_A + T_B dS_B, \qquad (43)$$

or since -p'$_A$ > p$_A$

$$T_{Ai} dS_A > -T_B dS_B \quad (44)$$

or

$$dS_A > \frac{dQ}{T_{Ai}}. \qquad (45)$$

VI. "Isothermal" Processes with final volume inferior then the isothermal reversible process .

The process that conducts the subsystem A to the minimum final volume, with the final temperature equal to the initial temperature, is the IRP (eq. (26)). This being so all the other processes , with the same final temperature $T_{Af} = T_{Ai}$, (and of course with the same final temperature for subsystem B) have the final volume V$_{Af}$ greater than the IRP volume. Therefore for all those processes $\Delta S_A \geq \Delta S_{A(IRP)}$ [16].

Therefore if the gas A is compressed connecting a heat reservoir with temperature T_{Ai}, leaving the volume of subsystem A to a value inferior then the volume of the reversible process (IRP), the energy introduced in the reservoir is higher then $\Delta U_B = C_{VB} (T_{Ai} - T_{Bi})$ since $W_{ext} = \int -p_{ext} dV > \Delta U_B$. If after this compression the reservoir is connected with subsystem B the energy that flows to B is ΔU_B. For this process, the total entropy change is

$$\Delta S = \Delta S_A + \Delta S_B + \Delta S_H = R\ln\left(\frac{V_{Af}}{V_{Ai}}\right) + C_{VB}\ln\left(\frac{T_{Ai}}{T_{Bi}}\right) + \frac{W_{ext} - \Delta U_B}{T_{Ai}}. \quad (46)$$

The entropy change that Belandria calculates (Belandria equation (16) at [15]) does not contain $\Delta S_H = \frac{W_{ext}-\Delta U_B}{T_{Ai}}$. This and inequality (42) completely explains the first controversy.

The final volume can not have the value proposed by Belandria because when the process is realized with sub-system A in contact with a reservoir at the same temperature T_{Ai} the energy conservation law ($\Delta U_{Res}=\Delta U_B$) and the entropy Law ($\Delta S_A+\Delta S_{Res}>0$) implies a greater volume then the volume proposed by Belandria.

VII. Interactions through a movable partition.

Lets consider that gas A and gas B occupy a constant total volume $V = V_A + V_B = const.$, separated by a movable piston. If the piston is blocked and if it is covered by an adiabatic film, the two subsystems, A and B, achieve a local equilibrium state. The initial volume and initial temperature for A and B, are respectively V_{Ai}, T_{Ai} and V_{Bi}, T_{Bi}.

The pressures are

$$p_{Ai} = \frac{RT_{Ai}}{V_{Ai}} \quad (47)$$

and

$$p_{Bi} = \frac{RT_{Bi}}{V_{Bi}}. \quad (48)$$

Lets apply to the piston an exterior force and simultaneously retire the adiabatic film. When an equilibrium point is reached, we have

$$W_{ext} = -p_{ext}\Delta V_A = \Delta U_A + \Delta U_B. \qquad (49)$$

If the final temperature for A is equal to the initial temperature T_{Ai}, we have $\Delta U_A = 0$ and

$$W_{ext} = \Delta U_B = C_{VB}(T_{Ai} - T_{Bi}), \qquad (50)$$

$$-p_{ext}(V_{Af} - V_{Ai}) = C_{VB}(T_{Ai} - T_{Bi}). \qquad (51)$$

For the equilibrium state, we must have an equilibrium for the pressures, for example

$$p_{ext} + p_{Bf} = p_{Af} \qquad (52)$$

or

$$p_{ext} + \frac{RT_{Ai}}{(v - v_{Af})} = \frac{RT_{Ai}}{V_{Af}}. \qquad (53)$$

Equations (51) e (53) allows to calculate V_{Af} and p_{ext}. The entropy changes for A and B are

$$\Delta S_A = R\ln\left(\frac{V_{Af}}{V_{Ai}}\right), \qquad (54)$$

$$\Delta S_B = R\ln\left(\frac{V - V_{Af}}{V_{Bi}}\right) + C_V \ln\left(\frac{T_{Af}}{T_{Ai}}\right). \qquad (55)$$

For this configuration it is not possible to obtain $\Delta S_B = \int \frac{dQ}{T_B}$. For this process the energy exchanged through the movement of the piston results from the collisions of the molecules of the gas. For this configuration it is not possible to separate a Q term. To clarify this matter it helps to consider the limiting case where the thermal conductivity of the piston is zero. We have the following equations :

$$dE_{Kin} + dE_{pot} + dU_A + dU_B = 0. \qquad (56)$$

$$dW_{ext} + dW_{int} + dE_{pot} + dU_A + dU_B = 0. \qquad (57)$$

and since $dW_{ext} = -dE_{pot}$

$$dU_A + dU_B = -dW_{int}, \qquad (58)$$

$$dU_A + dU_B = -p'_A dV_A - p'_B dV_B \quad , \qquad (59)$$

$$dU_A = -p'_A dV_A - p'_B dV_B - dU_B \quad , \qquad (60)$$

or

$$dU_A = -p'_A dV_A - p'_B dV_B + p_B dV_B - T_B dS_B \quad . \qquad (61)$$

If the process is reversible we must have $p'_B = p_B$ and $p'_A = p'_B$ and from (61)

$$dU_A = -p_A dV_A - T_B dS_B. \qquad (62)$$

Equation (61) is consistent with $dU_A = -p_A dV_A + T_A dS_A$, $T_A = T_B$ and $dS_A + dS_B = 0$.

If $dV_B = 0$, we have from (60)

$$dU_A = -p'_A dV_A - T_B dS_B \quad , \qquad (63)$$

which can be put with the form

$$dU_A = dW_A + dQ_A. \qquad (64)$$

dQ_A has, here a clear meaning, energy that flows between A and B through the partition (configuration 1)

If this is so lets consider initial conditions $T_{Ai} \neq T_{Bi},\ p_{ext} + p_{Bi} = p_{Ai}$.

We can admit an evolution of p_{ext} that imposes a constant temperature for A, T_{Ai} until the final equilibrium point was attained with $T_{Af} = T_{Ai} = T_{Bf}$. For this configuration it is not possible to calculate $\frac{Q}{T_{Ai}}$ and therefore it is not possible to calculate the entropy production, based on equation (40).

Finally, lets consider the other controversy [1-15]:

Gas A and gas B have equal initial pressures, and initial different temperatures. The movable piston, separating the two gases has zero thermal conductivity. A kinetic analysis [8-12] gives for the final equilibrium state, equal temperatures and equal pressures, that can be easily calculated. If we admit as true the relations $dS_{A,B} \geq \frac{dQ_{A,B}}{T_{A,B}}$ with $dQ_{A,B} = 0$ we must have $dS_{A,B} > 0$. But the subsystem which initially has an higher temperature , during the process decreases the temperature and therefore the volume, decreases the entropy. Therefore the relations $dS_{A,B} > 0$ can not be simultaneously verified. $dS_A + dS_B > 0$ can not be put on the form $dS_{A,B} \geq \frac{dQ}{T_{A,B}}$ [5-7, 10-14] with dQ equal to zero. This solves the other controversy.

Conclusion

In this work we analyse several irreversible processes arising from the interaction of two subsystems, for two configurations. When one of the subsystems has a constant volume the energy that flows from the other subsystem is identified with a heat term. For this case, the entropy production, results from the global entropy increase. If the interaction between the subsystems results from the movement of a piston that separates the two subsystems, the energy exchange between the subsystems can not have the same interpretation, the relation $dS_i > \frac{dQ_i}{T_i}$ can not be established. Therefore the motion of an adiabatic piston, when the initial pressures are equal and the temperatures different, satisfies the Second Law, with a decrease of the entropy of one of the subsystems and an increase of the entropy of the other. With this work we contribute to the solution of two controversies.

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