

# A Revised Interpretation of the Thermodynamic Theory Including the Einstein Mass-Energy Relation $E = mc^2$

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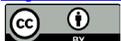
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## Abstract

Thermodynamics being among the most synthetic theories of physics and the mass-energy relation  $E = mc^2$  among the most general equations of science, it is somewhat surprising that this latter is not explicitly present in the laws of thermodynamics. Coupling this observation with the conceptual difficulties often felt in learning thermodynamics leads to the idea that both situations may have the same cause. On the basis of these clues, this paper is intended to provide complementary arguments to a hypothesis already presented. It consists of showing the existence of an imperfect compatibility between the conventional formulations of the first and second laws of thermodynamics and suggesting the need of the mass-energy relation to solving the problem.

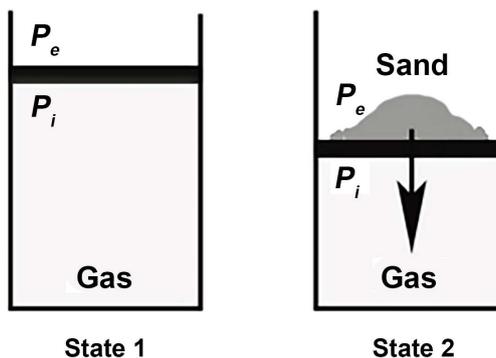
## Keywords

Thermodynamics, Entropy, Energy, Einstein's Mass-Energy Relation, Relativity

## 1. Introduction

### 1.1. Brief Review of the Concepts of Reversibility and Irreversibility

The system we are considering (**Figure 1**) is a gas contained in a cylinder permeable to heat (*i.e.* diathermal), and equipped with a mobile frictionless piston, which is also diathermal. In state 1, the external pressure  $P_e$  and the internal pressure  $P_i$  (pressure of the gas) have the same value  $P_1$ . Then, due to the deposition of a mass of sand on the piston,  $P_e$  passes from the value  $P_1$  to a value  $P_2$ , and the piston moves down with the consequence that, in state 2,  $P_i$  also reaches the value  $P_2$ .



**Figure 1.** Irreversibility and reversibility.

The sand can be deposited very rapidly (*i.e.* all at once) or very slowly (*i.e.* in several successive small batches).

In the first case,  $P_e$  reaches immediately the value  $P_2$ , while  $P_i$  reaches this value only when the piston stops. It is well known that this situation is designated irreversibility in the sense that  $P_e$  and  $P_i$  are always different during the process. In such conditions, the work done on the gas by the piston, for an elementary change in volume noted  $dV$ , must be written

$$dW_{irr} = -P_e dV \tag{1}$$

In the second case, by contrast, the pressure exerted by the piston passes very gradually from the initial value  $P_1$  to the final value  $P_2$ , with the consequence that, at each moment of the process,  $P_e$  and  $P_i$  can be considered as equal. This situation is designated reversibility and, in such conditions, the elementary work done on the gas, by the piston, is given by the relation:

$$dW_{rev} = -P_i dV \tag{2}$$

For a given value of  $dV$ , the difference between  $dW_{irr}$  and  $dW_{rev}$  takes the form:

$$dW_{irr} - dW_{rev} = dV(P_i - P_e) \tag{3}$$

that can also be written:

$$dW_{irr} = dW_{rev} + dV(P_i - P_e) \tag{4}$$

Referring to **Figure 1**, it appears that we have  $dV > 0$  when  $P_i > P_e$  and  $dV < 0$  when  $P_i < P_e$  (this second situation being the one illustrated by the diagram). As a consequence, the term  $dV(P_i - P_e)$  obeys in all cases the condition:

$$dV(P_i - P_e) > 0 \tag{5}$$

meaning itself that we have always:

$$dW_{irr} > dW_{rev} \tag{6}$$

Another possible expression of Equation (4) is therefore:

$$dW_{irr} = dW_{rev} + dW_{add} \tag{7}$$

where  $dW_{add}$  can be regarded as an additional energy representing the difference

between  $dW_{irr}$  and  $dW_{rev}$  and obeying the condition:

$$dW_{add} > 0 \tag{8}$$

In practice, it is well known that the additional energy, noted here  $dW_{adb}$  mainly appears in the form of heat, classically designated  $dQ$ , that is evacuated towards the surroundings. This heat evacuation explains that the final temperature of the gas has in fact the same value as its initial temperature, that is also the temperature of the surroundings.

### 1.2. Remarks Concerning the First Law of Thermodynamics

For the matter that will be discussed in this paper, the information we need about the first law is summarized in Equations (9), (10), (11), (12), and (13) given below.

The first law of thermodynamics is a postulate which consists in admitting that when a system passes from a determined state 1 to a determined state 2, its internal energy variation, noted  $dU$ , always obeys the relation:

$$dU_{irr} = dU_{rev} \tag{9}$$

If the energy exchanges are limited to work ( $W$ ) and heat ( $Q$ ), the detailed meaning of Equation (9) takes the form:

$$dW_{irr} + dQ_{irr} = dW_{rev} + dQ_{rev} \tag{10}$$

If the system taken in consideration is isolated, the complementary precision given by the first law is that Equations (9) and (10) become respectively:

$$dU_{irr} = dU_{rev} = 0 \tag{11}$$

$$dW_{irr} + dQ_{irr} = dW_{rev} + dQ_{rev} = 0 \tag{12}$$

Knowing that an isolated system has no exchanges of energy with its surroundings, all the terms of Equations (11) and (12) refer to energy exchanges occurring inside the system.

We have seen with Equation (6) that  $dW_{irr}$  and  $dW_{rev}$  obey the general relation:

$$dW_{irr} > dW_{rev} \tag{R.6}$$

Combining this data with the information given by Equations (9) and (10), leads to the conclusion that the terms  $dQ_{irr}$  and  $dQ_{rev}$  must themselves obey the relation:

$$dQ_{rev} > dQ_{irr} \tag{13}$$

In thermodynamic textbooks, the considerations concerning  $dQ$  are generally discussed in the chapters dealing with the second law. We will now enter in this context in order to see if the relation  $dQ_{irr} < dQ_{rev}$  given by Equation (13) can really be verified.

### 1.3. Remarks Concerning the Second Law of Thermodynamics

As was the case for the first law, the concepts of reversibility and irreversibility remain of fundamental importance for the understanding of the second law, but

they are associated here with the complementary concept called entropy. Its presentation is often done in the following condensed form.

**In conditions of reversibility**, a change in entropy (noted  $dS$ ) is linked to a change in heat ( $dQ$ ) and to the absolute temperature ( $T$ ) by the relation:

$$dS = dQ/T \tag{14}$$

**In conditions of irreversibility** the corresponding relation becomes:

$$dS > dQ/T \tag{15}$$

When we discover these equations for the first time and receive the complementary information that  $dS$  has the same value in both cases (because  $S$  is a state function, as well as  $V$ , the volume), we are tempted to think that  $dQ$  represents  $dQ_{rev}$  in Equation (14) and  $dQ_{irr}$  in Equation (15). With this idea in mind, we are led to deduce that these terms obey the relation:

$$dQ_{irr} < dQ_{rev} \tag{R. 13}$$

which is the one suggested by Equation (13), at the end of the previous section.

At this stage of the presentation, the reasoning seems coherent and easily understandable. The problem is that the relation  $dQ_{irr} < dQ_{rev}$  is not confirmed when we examine the numerical applications presented as examples of the use of these equations (one of them, very simple, is mentioned below in paragraph 2.2).

The reason is due to the fact that, in this context, we discover that the precise meaning of Equation (14) is really:

$$dS = dQ_{rev}/T_i \tag{16}$$

but the precise meaning of Equation (15) is interpreted as being:

$$dS = dQ_{rev}/T_e + dS_i \tag{17}$$

complemented by the information that the term  $dS_i$ , designated as the internal component of entropy, has always a positive value and therefore can always be written:

$$dS_i > 0 \tag{18}$$

A related piece of information is that the term  $dS = dQ/T_e$  is designated  $dS_e$  and called the external component of entropy, so that a condensed writing of Equation (17) is:

$$dS = dS_e + dS_i \tag{19}$$

Although the term  $dQ$  of Equation (15) is sometimes designated  $dQ_{irr}$  in thermodynamics textbooks, the numerical value given to  $dQ$  in Equation (17) is really  $dQ_{rev}$ , as will be seen further with Equation (28) that refers to a typical numerical example.

The conclusion which follows from this observation is that the term  $dQ_{irr}$  is not present in the equations going from number 14 to number 19, so that its comparison with the term  $dQ_{rev}$  is not possible at the moment.

The situation was different for the comparison between the terms  $dW_{irr}$  and

$dW_{rev}$  introduced in paragraph 1 because their definitions, given by Equations (1) and (2), were directly presented in the form of energy equations.

To obtain the conversion of the entropy equations (16) and (17) into energy equations, the solution consists in multiplying both terms of Equation (16) by  $T_p$  and the three terms of Equation (17) by  $T_e$ . The results are:

For Equation (16):

$$dQ_{rev} = T_i dS \tag{20}$$

For Equation (17)

$$T_e dS = dQ_{rev} + T_e dS_i \tag{21}$$

whose meaning is

$$dQ_{irr} = dQ_{rev} + T_e dS_i \tag{22}$$

In the same manner as, in Equation (7), we have designated  $dW_{add}$  the term representing the difference  $dW_{irr} - dW_{rev}$ , we can here adopt the designation  $dQ_{add}$  for the term  $T_e dS_p$ , so that an alternative writing of Equation (22) is:

$$dQ_{irr} = dQ_{rev} + dQ_{add} \tag{23}$$

Having noted with Equation (17) that  $dS_i$  is always positive and knowing that the same is true for  $T_i$  and  $T_e$  (because, in thermodynamics, temperatures are always expressed in Kelvin), the term  $T_e dS_p$ , also noted  $dQ_{add}$  is itself positive. Consequently, it can be derived from Equation (23) that  $dQ_{irr}$  and  $dQ_{rev}$  are linked together, not by the relation  $dQ_{irr} < dQ_{rev}$  presented above as the expected one (Equation (13)), but by the inverted relation, that is:

$$dQ_{irr} > dQ_{rev} \tag{24}$$

## 2. Discussion: Consequences of These Observations on the Understanding of the Theory

### 2.1. Preliminary Remark

If we accept the proposal  $dQ_{irr} > dQ_{rev}$  given by Equation (24) and at the same time the proposal  $dW_{irr} > dW_{rev}$  given by Equation (6), their addition leads to the proposal:

$$dW_{irr} + dQ_{irr} > dW_{rev} + dQ_{rev} \tag{25}$$

which disagree with the proposal  $dW_{irr} + dQ_{irr} = dW_{rev} + dQ_{rev}$  presented in Equation (10) as the conventional understanding of the first law of thermodynamics.

The situation is similar if the addition of Equations (24) and (6) is entered in Equations (11) and (12), because the result obtained would mean that an isolated system can be concerned by a positive variation of its internal energy ( $dU_{irr} > 0$ ).

Despite the fact that such a proposal appears impossible in the conventional approach of thermodynamics, it becomes easily understandable if the mass-energy relation is taken into account. Two reasons may explain why it has not been done previously. The first one is that at the time of the discovery of the laws of thermodynamics, the theory of relativity was not known. The second is

that even without the help of the mass-energy relation, the efficiency of the thermodynamic tool is indisputable, so that no urgency was felt to revise the interpretation of its laws. Nevertheless, it seems that the theory gets more easily understandable when this complement is added and perhaps the scope of its applications may be extended.

## 2.2. Analysis of a Heating Process Concerning a Closed System

For an easy approach of the matter, let us examine the situation below, presented in a basic thermodynamic course as an example of use of the concept of entropy. The system is defined as 1000 g of water (1 liter) that are heated from 20°C (293 K) to 80°C (353 K), by contact with a thermostat at 80°C (353 K), under atmospheric pressure. The asked question concerns the determination of the terms  $\Delta Q$ ,  $\Delta S$ ,  $\Delta S_e$  and  $\Delta S_b$ , knowing that the specific heat capacity of water is  $c_{p_{\text{water}}} = 4,184 \text{ JK}^{-1}\cdot\text{g}^{-1}$  that can be admitted constant over the temperature range.

The answers, equally given in the course, are as follows:

$$\Delta Q = \int_{T_1}^{T_2} mc_p dT = mc_p \Delta T = 1000 \times 4.184 (353 - 293) = 251040 \text{ J} \quad (26)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} = mc_p \ln \frac{T_2}{T_1} = 1000 \times 4.184 \ln \frac{353}{293} = 780 \text{ JK}^{-1} \quad (27)$$

$$\Delta S_e = \frac{\Delta Q}{T_e} = \frac{251040}{353} = 711 \text{ JK}^{-1} \quad (28)$$

$$\Delta S_i = \Delta S - \Delta S_e = 69 \text{ JK}^{-1} \quad (29)$$

So far, these results do not raise ambiguity whether the hypothesis to which we refer is the classical interpretation or the new suggested one. The divergence begins when the asked question is in knowing whether the term  $\Delta Q$ , mentioned in Equation (28) means  $\Delta Q_{irr}$  or  $\Delta Q_{rev}$ . The interest of the question comes from the fact that in the classical approach, the relation between both terms is the inequality  $dQ_{irr} < dQ_{rev}$  given by Equation (13), while in the new suggested hypothesis, it is the inequality  $dQ_{irr} > dQ_{rev}$  given by Equation (24).

In the first hypothesis, the question is considered useless for the example presently examined, because the formulation of the first law being  $dU_{irr} = dU_{rev}$ , it reduces to  $dQ_{irr} = dQ_{rev}$  when the energy exchange is limited to heat. This is practically the case here, since the work due to change in volume of the water heated from 20°C to 80°C can be considered negligible, compared to the change in heat, so that we can write  $dW = 0$ .

The situation is not the same in the second hypothesis because the conversion of the Entropy Equation (17) into the Energy Equation (21) introduces a real difference between  $dU_{irr}$  and  $dU_{rev}$  and consequently between  $\Delta Q_{irr}$  and  $\Delta Q_{rev}$  although the change in volume is always considered negligible.

To know the exact meaning of the term noted  $\Delta Q$ , the criterion to take into account is that its value is independent of the degree of irreversibility of the heating process when it represents  $\Delta Q_{rev}$ , while it is not the case when it represents  $\Delta Q_{irr}$ . To make a test using this criterion, we may imagine a division

of the heating process in two steps noted A and B, the first one from 293 K to 223 K, the second from 223 K to 253 K. Reproducing the calculation presented above and adding the obtained results, we are led to the following table:

$$\Delta Q = \Delta Q_A + \Delta Q_B = 125580 + 125580 = 251040 \text{ J} \quad (30)$$

$$\Delta S = \Delta S_A + \Delta S_B = 408 + 372 = 780 \text{ JK}^{-1} \quad (31)$$

$$\Delta S_e = \Delta S_{eA} + \Delta S_{eB} = 388.79 + 355.75 = 744 \text{ JK}^{-1} \quad (32)$$

$$\Delta S_i = \Delta S_{iA} + \Delta S_{iB} = 19.4 + 16.42 = 36 \text{ JK}^{-1} \quad (33)$$

Through these results, it can be effectively observed that the division of the heating process in two steps has no effect on the values of  $\Delta Q$  and  $\Delta S$ , but increases the value of  $\Delta S_e$  (change from 711 to 744  $\text{JK}^{-1}$ ) and decreases that of  $\Delta S_i$  (change from 69 to 36  $\text{JK}^{-1}$ ). If the number of steps is multiplied, we easily conceive that the value  $\Delta S_i$  tends progressively towards zero, meaning that the heating process tends towards reversibility. The question asked above is therefore answered in the sense that  $\Delta Q$  represents here  $\Delta Q_{rev}$  and the corresponding term  $\Delta Q_{irr}$  can be calculated by Equation (22), whose differential and integrated formulations are respectively:

$$dQ_{irr} = dQ_{rev} + T_e dS_i \quad (R. 22)$$

$$\Delta Q_{irr} = \Delta Q_{rev} + T_e \Delta S_i \quad (34)$$

Applying Equation (34) to the considered system leads to the following observations:

When the heating process is done in a single step, we have:

$$\Delta Q_{irr} = 251040 + 353 \times 69 = 275397 \text{ J} \quad (35)$$

When it is done in two steps, we have:

$$\Delta Q_{irr} = (125520 + 323 \times 19.4) + (125520 + 353 \times 16.42) = 263102 \text{ J} \quad (36)$$

Being lower than the previous one, this last value concerns effectively the term  $\Delta Q_{irr}$  which decreases progressively and tends towards  $\Delta Q_{rev}$  (itself remaining constant) when the number of steps is multiplied. Thanks to this difference of behavior, the problem of the identification of  $\Delta Q_{irr}$  and  $\Delta Q_{rev}$  is solved.

The reason why this procedure is not used in thermodynamic courses is evidently that the conclusion  $\Delta Q_{irr} > \Delta Q_{rev}$  to which it leads it is not in accordance with the usual understanding of the first law. As mentioned above, this last one implies the general equality  $\Delta U_{irr} = \Delta U_{rev}$  which becomes  $\Delta Q_{irr} = \Delta Q_{rev}$  when the energy exchange is limited to heat, as it is the case here. Referring to this situation, it can be observed that the strict obedience to the conventional understanding of the first law reduces the information given by the second law, because it does not allow the conversion of the entropy Equation (17) to the energy Equation (21). In close relation with this remark, some additional suggestions are discussed below.

If we group together Equations (20), (21) and (22) which are respectively:

$$dQ_{rev} = T_i dS \quad (R. 20)$$

$$T_e dS = dQ_{rev} + T_e dS_i \quad (R. 21)$$

$$dQ_{irr} = dQ_{rev} + T_e dS_i \quad (R. 22)$$

we see that the terms  $dQ_{irr}$  and  $dQ_{rev}$  can be directly defined by the energy formulations:

$$dQ_{irr} = T_e dS \quad (37)$$

$$dQ_{rev} = T_i dS \quad (38)$$

The entropy being a state function, as the volume, the differential  $dS$  has the same value in both equations. Therefore we can write:

$$dQ_{irr} - dQ_{rev} = dS(T_e - T_i) \quad (39)$$

*i.e.*

$$dQ_{irr} = dQ_{rev} + dS(T_e - T_i) \quad (40)$$

The terms  $T_e$  and  $T_i$  being positive (absolute temperatures), we also see from Equations (37) and (38) that  $dS$  and  $dQ$  have the same sign. The term  $dQ$  being positive when  $T_e > T_i$  and negative when  $T_e < T_i$ , the same is true for  $dS$ . Consequently, the term  $dS(T_e - T_i)$  is always positive, confirming the relation:

$$dQ_{irr} > dQ_{rev} \quad (R. 24)$$

As already done for  $dW_{irr}$  with Equation (7), we can give to this last equation the expression:

$$dQ_{irr} = dQ_{rev} + dQ_{add} \quad (41)$$

where the term  $dQ_{add}$  is positive.

Then adding the relations  $dQ_{irr} = dQ_{rev} + dQ_{add}$  (Equation (41)) and  $dW_{irr} = dW_{rev} + dW_{add}$ , (Equation (7)), we get the global result:

$$dU_{irr} = dU_{rev} + dU_{add} \quad (42)$$

whose meaning is:

$$dU_{irr} > dU_{rev} \quad (43)$$

### 2.3. Analysis of a Heat Exchange Occurring inside an Isolated System

Let us imagine now, the case of an isolated system made of two parts 1 and 2 separated by a diathermic wall. Supposing that part 1 is defined as 1 liter of water at 20°C and part 2 as 1 liter of water at 80°C, our objective is the analysis of their exchange of energy.

A first idea that comes to mind is that, just after the end of this exchange, both parts will be at the same final temperature  $T_f = 50^\circ\text{C}$ , ( $= 323\text{ K}$ ). If a thermometer is placed in each of them, this result can be verified directly, but can also be predicted by the well-known equation:

$$T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2} \quad (44)$$

which gives  $T_f = 323\text{ K}$  (taking into account that  $C_1 = m_1 c_1$  and  $C_2 = m_2 c_2$ ).

Designating  $T_i$  the initial temperature and  $T_f$  the final temperature, the main elements of the calculation are given below.

For the terms  $\Delta Q_{rev1}$ ,  $\Delta Q_{rev2}$  and  $\Delta Q_{rev\ syst}$  we get:

$$\Delta Q_1 = C_1 (T_{f1} - T_{i1}) = 4184(323 - 293) = 125520 \text{ J} \tag{45}$$

$$\Delta Q_2 = C_2 (T_{f2} - T_{i2}) = 4184(323 - 353) = -125520 \text{ J} \tag{46}$$

$$\Delta Q_{rev\ syst} = \Delta Q_{rev1} + \Delta Q_{rev2} = 125520 - 125520 = 0 \tag{47}$$

For the terms  $\Delta S_1$ ,  $\Delta S_2$  and  $\Delta S_{syst}$ :

$$\Delta S_1 = \int_{T_{i1}}^{T_{f1}} C_1 \frac{dT}{T} = C_1 \ln \frac{T_{f1}}{T_{i1}} = 1000 \times 4.184 \ln \frac{323}{293} = 408 \text{ JK}^{-1} \tag{48}$$

$$\Delta S_2 = \int_{T_{i2}}^{T_{f2}} C_2 \frac{dT}{T} = C_2 \ln \frac{T_{f2}}{T_{i2}} = 1000 \times 4.184 \ln \frac{323}{353} = -372 \text{ JK}^{-1} \tag{49}$$

$$\Delta S_{syst} = \Delta S_1 + \Delta S_2 = 408 - 372 = 36 \text{ JK}^{-1} \tag{50}$$

For the terms  $T_1^*$  and  $T_2^*$  representing the average temperatures of part 1 and part 2:

$$T_1^* = \frac{\Delta Q_{rev1}}{\Delta S_1} = \frac{125520}{408} = 308 \text{ K} \tag{51}$$

$$T_2^* = \frac{\Delta Q_{rev2}}{\Delta S_2} = \frac{-125520}{-372} = 338 \text{ K} \tag{52}$$

For the terms  $\Delta Q_{irr1}$ ,  $\Delta Q_{irr2}$  and  $\Delta Q_{irr\ syst}$ :

$$\Delta Q_{irr1} = \int_{S_1}^{S_2} T_{e1} dS = T_{e1}^* \Delta S_1 = T_2^* \Delta S_1 = 338 \times 408 = 137904 \text{ J} \tag{53}$$

$$\Delta Q_{irr2} = \int_{S_1}^{S_2} T_{e2} dS = T_{e2}^* \Delta S_2 = T_1^* \Delta S_2 = 308 \times (-372) = -114576 \text{ J} \tag{54}$$

$$\Delta Q_{irr\ syst} = \Delta Q_{irr1} + \Delta Q_{irr2} = 137904 - 114576 = 23328 \text{ J} \tag{55}$$

In the conventional approach of the theory, the only results taken in consideration for the whole system are  $\Delta Q_{syst} = 0$  (Equation (47)), where  $\Delta Q_{syst}$  means indifferently  $\Delta Q_{rev\ syst}$  or  $\Delta Q_{irr\ syst}$  and  $\Delta S_{syst} = 36 \text{ JK}^{-1}$  (Equation (50)).

In the revised approach that is proposed here, we see that a distinction is made between the term  $\Delta Q_{rev\ syst} = 0$ , and the term  $\Delta Q_{irr\ syst} > 0$ , whose calculated value is  $\Delta Q_{irr\ syst} = 23328 \text{ J}$ .

The reader accustomed to the usual approach of the theory may be tempted to consider this last result as unrealistic, because it seems impossible that an energy can be created inside an isolated system. Before examining below the possibility of a link between thermodynamics and relativity, the attention is called to the following remark, briefly evoked in the abstract.

Taking into account that thermodynamics is among the most synthetic theories of physics and the relation  $E = mc^2$  among the most general equations of science, we may be astonished that this latter is not explicitly present in the laws of thermodynamics. Perhaps it is hidden behind our habit of giving the first law the meaning  $dU_{irr} = dU_{rev}$  instead of  $dU_{irr} > dU_{rev}$ ? It is on the basis of this idea

that the considerations discussed in the following paragraph are based.

### 3. The Link between Thermodynamics and Relativity

The first evocation of a link between thermodynamics and relativity seems to have been advanced by R. C. Tolman in 1928 [1]. At the sight of a photo nowadays presented in Wikipedia [2], one can imagine that he had the opportunity to discuss this subject with A. Einstein, all the more that they were co-authors of several articles. In the following years, many other authors have published on the same topic, their contributions being generally addressed to readers having a strong background in physics and mathematics. Some recent ones, quoted below in the section References, were written by H. Callen and G. Horwitz [3], Y. Rengui [4], S. A. Haywards [5], C. A. Farias, P. S. Moya and V. A. Pinto ([6], M. Requart [7], R. C. Gupta, R. Gupta and S. Gupta [8], T. Yarman, A. L. Kholmetskii and J-L Tane [9], V. Krasnoholovets and J-L. Tane [10].

From the observations reported in the present paper, the first information to keep in mind is that there is always a difference between the terms  $dQ_{irr}$  and  $dQ_{rev}$ , even when the energy exchange concerning the considered system is limited to heat. The second information is that this difference always obeys the condition  $dQ_{irr} > dQ_{rev}$ . Added to the condition  $dW_{irr} > dW_{rev}$  (Equation (6)), we get the relation  $dU_{irr} > dU_{rev}$  (Equation (43)) which seems more appropriate than the proposal  $dU_{irr} = dU_{rev}$  (Equation (9)) in the role of fundamental postulate attached to the first law.

The hypothesis already suggested in several papers (J-L. Tane [11] [12] [13] [14] [15]) is that the inequality  $dQ_{irr} > dQ_{rev}$ , written above (Equation (41)) under the expression:

$$dQ_{irr} = dQ_{rev} + dQ_{add} \quad (\text{R. 41})$$

can be interpreted as having the meaning:

$$dU_{irr} = dU_{rev} \pm c^2 dm \quad (56)$$

where  $c^2 dm$  is the differential form of the mass-energy relation  $E = mc^2$ . The sign  $\pm$  means that the choice between + and - is not done for the moment and will be examined further.

The term  $dU_{add}$  having been described above as omnipresent in thermodynamic processes, its assimilation to the term  $c^2 dm$  is a way to say that thermodynamics and relativity are closely associated. In science education, this idea is not yet totally integrated. This can be seen from the fact that processes involving a detectable change in mass, such as nuclear reactions, are rarely interpreted from a thermodynamic point of view. Correlatively, numerical examples presented in thermodynamics books are almost never devoted to nuclear reactions.

This situation reminds us that thermodynamic systems are classically divided into three categories, depending on whether they are open, closed, or isolated. Before the discovery of relativity, it was admitted that only open systems can be affected by a change in mass. After this discovery, the same possibility has been

extended to closed systems. Perhaps will it be equally extended to isolated systems in the future?

In a book of thermodynamics for earth scientists recently written by G. M. Anderson [16], the mass-energy relation  $E = mc^2$  is mentioned, with the remark that its practical use is mostly impossible, since the changes in mass are too small to be measurable. Referring to the context evoked above (isolated system made of two liters of water designated 1 and 2 that have a mutual heat exchange) there is no doubt that the change in mass is not detectable. Despite this state of affairs, the problem seems of great interest from the theoretical point of view.

The starting reason is that the change in mass that can be predicted is not the same, depending on whether we adopt the classical approach of the theory or the new suggested one. In the first case, the heat exchange will be characterized by the relation  $\Delta Q_1 = -\Delta Q_2$ , (Equations (45) and (46)) implying  $\Delta m_1 = -\Delta m_2$  and consequently  $\Delta m_{\text{sys}} = 0$ . In the second case, having obtained  $\Delta Q_{\text{irr}1} \neq -\Delta Q_{\text{irr}2}$  (Equations (53) and (54)), we will get  $\Delta m_{\text{sys}} \neq 0$  and the remaining question is the choice between  $\Delta m_{\text{sys}} > 0$  and  $\Delta m_{\text{sys}} < 0$  for the corresponding change in mass.

In the same way as, in paragraph 1, the energy initially designated  $dW_{\text{add}}$  (Equation (8)) was not really work, but heat, the energy noted  $\Delta Q_{\text{irr sys}} = 23328 \text{ J}$  (Equation (56)) is not really heat but another kind of energy. It is not heat because the experimenters never reported that an exchange of heat between two parts of an isolated system have led to a final temperature exceeding the value given by Equation (44). Being generated inside the system, the possible solution is that  $\Delta Q_{\text{irr sys}}$  is a potential energy of gravitation, whose origin is a decrease in mass of the system. Referring to the mass-energy relation this explanation corresponds to the formulation  $dE = -c^2 dm$  which means that Equation (56) would itself be written:

$$dU_{\text{irr}} = dU_{\text{rev}} - c^2 dm \quad (57)$$

This equation would keep the same form for a system containing other materials than water. Transposed at the scale of a very large system, the presence of the term  $c^2 dm$ , implies a possible gravitational effect, which cannot be taken into account when the basis for discussion is the equality  $dU_{\text{irr}} = dU_{\text{rev}}$  instead of Equation (57). Preliminary comments concerning this question are presented in reference [15], with the possibility that the decrease in mass contributes to increase the Earth-Moon distance. Correlatively, the possibility is evoked in reference [17] that, for living systems, Equation (57) could be substituted by equation:

$$dU_{\text{irr}} = dU_{\text{rev}} + c^2 dm \quad (58)$$

Remaining in the context of systems made of inert matter (objects of the experiments that have inspired the laws of thermodynamics), another interesting question is the relation between  $c^2 dm$  and the function Gibbs Free Energy. Designated  $G$ , in honor of its discoverer Josiah Willard Gibbs, its definition is:

$$G = U + PV - TS \quad (59)$$

giving, by differentiation:

$$dG = dU + d(PV - TS) \quad (60)$$

which can also be written:

$$dG = dU - d(TS - PV) \quad (61)$$

From the analysis presented above, the meaning of Equation (61) can be imagined as being:

$$dG = dU_{rev} - dU_{irr} \quad (62)$$

whose detailed writing becomes:

$$dG = (T_i dS - P_i dV) - (T_e dS + S dT_e - P_e dV - V dP_e) \quad (63)$$

If the considered process is carried out at constant temperature  $T_e$  and constant pressure  $P_e$ , the terms  $dT_e$  and  $dP_e$  are nil and this last equation is reduced to:

$$dG = (T_i dS - P_i dV) - (T_e dS - P_e dV) \quad (64)$$

whose condensed formulation is really:

$$dG = dU_{rev} - dU_{irr} \quad (65)$$

Then knowing from Equation (57) that  $dU_{irr} = dU_{rev} - c^2 dm$  and entering this value in Equation (65), we get for the precise meaning of  $dG$ :

$$dG = c^2 dm \quad (66)$$

For reason of convenience, the practical use of the term  $dG$  is not the one given by relation  $dG = dU_{rev} - dU_{irr}$  (Equation (65)) but by a relation that can be written very schematically:

$$dG = dU_{ref} - dU_{real} \quad (67)$$

where “ref” means “references” and “real” means “real”. In the study of chemical reactions, the conditions of references are generally  $T = 298$  K and  $P = 1$  bar.

Although the term  $c^2 dm$  is not explicitly written in equations such as 65 or 67, it is always implicitly present since  $dU_{irr} = dU_{rev} - c^2 dm$  (Equation (57)) and therefore it plays a fundamental role for the understanding of the thermodynamic theory.

Among the recent books intended to underline the omnipresence of equation  $E = mc^2$  around us and in the universe, is that of C. Galfard [18].

#### 4. Conclusions

Because my scientific specialty is not physics, but geology, I discovered thermodynamics late and with the precious help of books specially written for geologists. I have greatly appreciated that in some of them [19] [20], the idea was evoked that perhaps something remains to be clarified in the theory. As already noted, the existence of a link between thermodynamics and relativity seems all the more probable that the mass-energy relation  $E = mc^2$  is known to be one of the most

general equations of science while, in the same time, it is almost never used in thermodynamics textbooks.

Being limited to the macroscopic approach of thermodynamics, and the use of a basic mathematical tool, the hypothesis suggested in this paper seems easily accessible to a wide scientific readership. My hope is that it can be recognized useful by specialists and that the conversion of the entropy Equation (17) into the energy Equation (21) can be accepted in the future by authors of thermodynamics textbooks.

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### Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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