Evidence for a Close Link Between the Laws of Thermodynamics and the Einstein Mass-Energy Relation

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Abstract: After recalling the conceptual difficulty that is encountered in thermodynamic theory, the aim of this paper is to show that solving the problem requires a close correlation between the classical laws of thermodynamics and the Einstein mass-energy relation. The resulting idea is that the condition of evolution within a system, usually interpreted as an increase in entropy, must be extended to an increase in internal energy, itself related to a disintegration of mass. This new concept gives the theory a better coherence and opens a bridge between the field of thermodynamics and that of gravitation.

Keywords: laws of thermodynamics, energy, entropy, Einstein's mass-energy relation, gravitation.

1. INTRODUCTION

It is well known that while being very efficient in practice, the thermodynamic tool remains difficult to understand from the theoretical point of view. It is also well known that the difficulties encountered are not mathematical, but rather conceptual, and that they are perceived by those who have to learn thermodynamics as well as by those who have to teach it. Geology being now among the sciences that use thermodynamics for solving some specific problems, earth scientists have discovered, after others, the reality of this situation. They can greatly appreciate that in some books of thermodynamics, especially written for them, the reality of the conceptual difficulty is openly and rapidly evocated rather than cancelled as a forbidden subject. One of the best examples is that given by Nordström and Munoz[1] who related, in the preface of their book, the following opinion of the great physicist Arnold Sommerfeld about thermodynamics:

"The first time I studied the subject, I thought I understood it except for a few minor points.

The second time, I thought I didn't understand it except for a few minor points.

The third time, I knew I didn't understand it, but it did not matter, since I could use it effectively."

Another book intended for geologists and emphasizing the same conceptual problem is that of Anderson and Crerar[2]. Amid the quotations they relate is one of Reiss (page 3) recording his conviction that nobody understands thermodynamics completely. Another one is from Dickerson (page 295) who also notices the possibility of knowing thermodynamics without understanding it.

Coming from renowned specialists, these remarks must evidently be regarded as messages of high scientific signification.

2. THE PRECISE LOCATION OF THE CONCEPTUAL DIFFICULTY

To avoid complications that are not directly linked to the given problem, let us consider a thermodynamic system where the energy exchanges are limited to heat and the so-called "PV work". As a starting point, we recall that the main relation we have to examine, and which is a synthesis of the first, second, and third laws of thermodynamics is given by the expression:

$$\delta Q + \delta W = dU \leq TdS - PdV \qquad (1)$$

In this formula (often presented in two or three separated relations) the symbols refer to the system which is considered and has the following meanings : U (internal energy), S (entropy), V (volume), T (absolute temperature), P (pressure), Q (heat exchanged), W (work exchanged). The letter d indicates an exact differential since it designates the elementary variation of a state function such as U, S or V. To the contrary, the letter d indicates a non-exact differential since it designates the variation of a non-state function (except in particular conditions) such as Q or W.

In conditions of reversibility, the energized quantities δQ and δW are respectively equivalent to TdS and - PdV, and can therefore be represented by the expressions:

$$\delta Q = dQ = TdS \qquad (2)$$

$$\delta W = dW = - PdV \qquad (3)$$

The conceptual difficulty of thermodynamics comes from the fact that in order for it to be used with success, equation (1) must be worked in a way that does not seem logical. Theoretically, since dU is the exact differential of the state function U, the sum $\delta Q + \delta W$ would have the same numerical value as the sum $TdS - PdV$, whether the process involved is reversible or irreversible. Practically, it does not seem true, since the efficiency of the tool - that is its ability to confirm or predict experimental results - implicates that $\delta Q + \delta W$ would be less than $TdS - PdV$ for an irreversible process. Such a particularity explains that, in relation (1), the sign that appears between dU and $TdS - PdV$ is written "$\leq$" and not "=", but the physical reason for this situation remains mysterious.

In order to see what kind of solution can answer the problem, let us reexamine the interpretation of very simple processes and try to locate precisely the litigious point of our classical reasoning. For the clarity of the discussion, relation (1) is better separated in two possibilities whether it corresponds to the theoretical expression or to the practical one. They are respectively:

$$\text{Theoretical expression: } \delta Q + \delta W = dU = TdS - PdV \qquad (4)$$

$$\text{Practical expression: } \delta Q + \delta W = dU < TdS - PdV \qquad (5)$$

3. RECALLING THE INTERPRETATION OF A WORK EXCHANGE

We consider the well-known Joule experiment, which is an isolated system divided in two parts, 1 and 2. A gas is initially confined in part 1, while part 2 has been evacuated. After liberating the piston separating the two parts, the gas expands into the whole system. The thermodynamic interpretation of this process is very classical and generally regarded as the only possible solution. We recall it briefly hereunder.

A. Classical Interpretation

By reference to equation (1) and defining the system as the gas itself, the classical interpretation is the following: $\delta Q = 0$ because the global system is isolated, and inside it, the gas cannot exchange heat with a vacuum. And $\delta W = 0$ for the same reasons. We observe effectively that according to the general relation $dW = -P_e dV$ (where P_e designates the external pressure), the expansion of the gas inside the vacuum leads to the expression $\delta W = -P_2 dV$. The value of P_2 being zero, since it designates the pressure of the vacuum, we obtain $\delta W = 0$.

Having noted that δQ, δW, and consequently dU are zero, the classical interpretation consists in writing $TdS - PdV = 0$ and concluding $dS = (PdV)/T$. Since all the terms of this last equation are parameters of the system (none of them refers to the vacuum), the values of $P,\ T,$ and dV are all

positive, so that dS is positive too.

While this result is considered in good accordance with the second law of Thermodynamics (which states the condition $dS > 0$ for an isolated system concerning an internal irreversible process) there is a point not perfectly clear regarding the way it has been obtained. Crossing from $dU = 0$ to $TdS - PdV = 0$ implicates the use of equation (4), that is of a thermodynamic tool that theoretically would be appropriate, but practically is known as not being such, since gas expansion in a vacuum is an irreversible process.

B. Other Possible Interpretation

We define the system as being part 1 (the gas) and part 2 (the vacuum), instead of part 1 only. Concerning the heat exchange and for the reasons recalled above, we can write $dQ_1 = 0$ and $dQ_2 = 0$, so that for the global system, we obtain $dQ = 0$.

Concerning the work exchange, the general equation $dW = - P_e\, dV$ gives us respectively $dW_1 = - P_2\, dV_1$, whose value is zero as already seen, and $dW_2 = - P_1\, dV_2$, whose value is positive since P_1 (the pressure of the gas) is positive and dV_2 (the volume variation of the vacuum) is negative. The volume change for the whole system being $dV = 0$, we have necessarily $dV_2 = - dV_1$ so that dW_2 can also be written $dW_2 = P_1\, dV_1$.

Adding the two contributions we are led to the conclusion that for the global system, the energy result is $dU = P_1\, dV_1$, which consequently has a positive value. Of course, a question that may be asked is how can we conceive a positive value for dU in the case of an isolated system? The only possible answer is given by the Einstein mass-energy relation $E = mc^2$ which provides the possibility that an energy would be created in an isolated system by disintegration of its mass. In such a case, dQ, dW, and dU have indeed a value zero (at the scale of the whole system), and the positive energized quantity that must be taken into account is produced within the system itself.

By differentiation and since c (the speed of light) is a constant, the Einstein relation gives:

$$dE = c^2\, dm \tag{6}$$

Knowing that a decrease in mass induces an increase in energy, and conversely equation (6) is better written under the form:

$$dE = - c^2\, dm \tag{7}$$

Transposed in relations (1), (4), and (5), where the term dU has the signification dU_e (the energy exchanged between the system and its surroundings), dE can receive the designation dU_i (the energy created or destroyed inside the system according to the Einstein's mass-energy relation).

Rewriting relations (4), (5), and (1) would therefore give them the respective forms (8), (9), and (10), that are:

$$\text{- rev:} \quad \delta Q + \delta W \quad = \quad dU_e \qquad\qquad = \quad TdS - PdV \qquad\qquad (8)$$

$$\text{- irr:} \quad \delta Q + \delta W \quad < \quad dU_e + dU_i \quad = \quad TdS - PdV - c^2\,dm \qquad (9)$$

$$\text{- gen:} \quad \delta Q + \delta W \quad \leq \quad dU_e + dU_i \quad = \quad TdS - PdV - c^2\,dm \qquad (10)$$

where "rev," "irr," and "gen" mean reversible, irreversible and general.

For convenience, it may be useful to introduce the concept dU^* which is defined as:

$$dU^* = dU_e + dU_i \qquad\qquad (11)$$

dU^* can be designated as the "global energy change of the system," dU_e being the "external energy change" and dU_i the "internal energy change." We must be careful that in the classical language of thermodynamics, the internal energy change, noted as dU, corresponds to dU_e and not to dU_i (perhaps a designation such as "induced energy change" would be more appropriate for dU_i in order to avoid confusion).

Comparing relations (1), (4), and (5) with their respective homologues (10), (8), and (9) gives an answer to the conceptual problem evocated above. The understanding of this answer is easy when we reexamine the evolution of the system evocated before (the Joule experiment).

We have defined the system as including both part 1 (the gas) and part 2 (the vacuum), the whole being isolated. At the scale of the global system we may therefore write: $\delta Q = 0,$ $\delta W = 0, dUe = 0$ and $dV = 0$. Introducing this information in relation (9), leads to:

$$0 + 0 < 0 + dU_i = TdS - 0 - c^2 dm$$

Knowing that $dU_i = -c^2 dm$ and that T is positive, we have for the considered system:

$$dS = 0 \tag{12}$$

and relation (9) is reduced to:

$$dU_i = -c^2 dm \tag{13}$$

So we are led to the idea that the condition of evolution of the considered system would not be $dS > 0$, but $dU_i > 0$, implicating $dm < 0$.

The introduced modification concerns the interpretation given to the process, but not the usefulness of the thermodynamic tool, which remains unchanged and uncontested. For the latter reason, it is not necessary to introduce modifications in the usual conventions of language that give dS a positive value. Referring to relation (9), the solution for maintaining this result would consist of counting the energized quantity $-c^2 dm$ under the designation TdS (implicating by compensation that we would write zero under the designation $-c^2 dm$). When applying such a procedure to the whole system considered here, the significance of relation (9) becomes:

$$\delta Q + \delta W \quad < \quad dU_e + dU_i \quad = \quad TdS - PdV - c^2\, dm$$

$$0 + 0 \quad < \quad 0 + P_1\, dV_1 \quad = \quad TdS - 0 - 0$$

Doing so, we see that the value accepted to dS remains the same as usually given, that is $dS = P_1\, dV_1 /T$, where T means T_1 (since the concept of temperature has no significance in the vacuum). The important point is in taking into account the reality of the energized quantity dU_i whose value is $dU_i = P_1\, dV_1$ and not $dUi = 0$ as usually admitted.

In a more general way, for an isolated system composed of two gaseous parts separated by a thermostatic mobile piston and having initial pressures P_1 and P_2, the energized result obtained when adding the two mechanical contributions takes the form:

$$dW = dV_1\ (P_1 - P_2) \tag{14}$$

The natural evolution of the system being - at least in our near universe - a reduction of volume for the part with the lower initial pressure, we have $dW > 0$, and the only available explanation, as already seen, is given by the Einstein mass-energy relation that implicates:

$$dW \;=\; dUi \;=\; -\; c^2 dm \qquad\qquad\qquad (15)$$

Observing, in relation (14,) that the equality $P_1 = P_2$ would induce a value zero for dW, we are led to the general following idea:

A reversible process is characterized by the condition $dU_i = 0$ that implicates $dm = 0$ and represents an extension of the usual expression $dS_i = 0$.

An irreversible process is characterized by the condition $dU_i > 0$ that implicates $dm < 0$ and represents an extension of the usual expression $dS_i > 0$.

Evidently, when the relation in (14) P_1 and P_2 are not equal, the temperature increases in the gaseous part having the lower initial pressure and decreases in the other part. Therefore, the work exchange is itself completed by a heat exchange and the problem lies in knowing whether they necessarily balance one another as admitted in the classical interpretation of the first law of thermodynamics. For examining the matter in question, we shall consider next the interesting case of a heat exchange that is not accompanied by a work exchange.

4. RECALLING THE INTERPRETATION OF A HEAT EXCHANGE

The discussion concerning a heat exchange has the same general basis as those recalled - or proposed - when analyzing the previous example.

For a reversible process:

The classical formula (C F) and the new suggested formula (S F) are respectively:

$$- \text{C F:} \qquad \delta_Q \;+\; \delta_W \;=\; dU \;=\; TdS \;-\; PdV \qquad\qquad (4)$$

$$- \text{S F:} \qquad \delta_Q \;+\; \delta_W \;=\; dU_e \;=\; TdS \;-\; PdV \qquad\qquad (8)$$

For an irreversible process:

They are respectively:

$$- \text{C F:} \qquad \delta Q + \delta W = dU \qquad < \quad TdS - PdV \qquad (5)$$

$$- \text{S F:} \qquad \delta Q + \delta W < dU_e + dU_i = TdS - PdV - c^2 dm \qquad (9)$$

Let us consider a system defined as a given mass of water which is heated from an initial temperature T_1 to a final temperature T_2. The variation of volume being negligible, the terms PdV and dW can be eliminated. Thus δQ becomes equivalent to the exact differential dU (called dU_e in the new suggested formulation) and may be written dQ. Relations (4), (8), (5), and (9) therefore take on these respective reduced forms:

For a reversible process:

$$- \text{C F:} \qquad dQ = dU = TdS \qquad (16)$$

$$- \text{S F:} \qquad dQ = dU_e = TdS \qquad (17)$$

For an irreversible process:

$$- \text{C F:} \qquad dQ = dU \qquad < \quad TdS \qquad (18)$$

$$- \text{S F:} \qquad dQ < dU_e + dU_i = TdS - c^2 dm \qquad (19)$$

Since dQ, here, is an exact differential, the total thermal energy received by the system has the same numerical value, which can be noted ΔQ, whether the process of heating is reversible or irreversible. Knowing that $dQ = C\,dT$, where C designates the thermal capacity of the system (without a significant difference between C_p and C_v, since the system is condensed), ΔQ is given by the relation:

$$\Delta Q = \int_{T_1}^{T_2} C \, dT = C^* \int_{T_1}^{T_2} dT = C^* \left(T_2 - T_1 \right)$$

(20)

In relation (20) C^* is the mean value of C on the interval of integration and ΔQ can be identified with ΔU (which would then receive the designation ΔU_e in the new suggested formulation).

Returning to relations (5) and (9), more precisely to their right hand terms, it can be easily expected that the interpretation of an irreversible process of heating would not be exactly the same whether the existence of dU_i (equivalent to $-c^2 dm$) is recognized or not. The difference can be summarized as will be discussed next.

A. Classical interpretation

We must recall what has been seen in part 2 concerning the conceptual difficulty of thermodynamics. Theoretically, relation (4) would constitute an appropriate expression for both reversible and irreversible processes, but practically it is not true and the study of irreversible processes needs the use of relation (5).

Transposed upon the heating process examined here, relation (16) is the one which, theoretically, would be appropriate for both reversible or irreversible conditions and relation (18) is the one which is practically needed for irreversible conditions.

When the considered system is heated from a state 1 (temperature T_1) to a state 2 (temperature T_2), the integration of equations (16) and (18) gives respectively:

- rev: $$\Delta Q_1^2 = \Delta U_1^2 = T^* \Delta S_1^2$$ (21)

- irr: $$\Delta Q_1^2 = \Delta U_1^2 < T \Delta S_1^2$$ (22)

In (21), the term T^* can be called the mean value of T during the heating process and may be regarded as a state parameter of the system, being the ratio $\Delta U / \Delta S$, where both U and S are state functions. More accurately, T^* is a "space-time state parameter" in the sense that it represents the mean value of local temperatures that not only change with time, but for a given instant are not homogeneous in space.

Looking at relations (21) and (22) and knowing that U is a state function (having the signification

U_e), $\Delta U_1^{\prime 2}$ has necessarily the same value whether the conditions of heating are reversible or not and a similar observation can be made concerning $\Delta S_1^{\prime 2}$. Consequently, the coherence between the two relations implicates that the signification and the value given to T in (22) are not the same as that given to T^* in (21). For anyone having some practice in thermodynamics, this is evidence, since T in (22) means T_e (the external temperature) as recalled with the numerical examples considered further. Is it sufficient to conclude that therefore there is no problem? The answer is no, because the obtained coherence is mathematical, not physical. When admitting that the numerical value of T in (22) is higher than that of T^* in (21), we admit implicitly that the energized quantity $T \Delta S_1^{\prime 2}$ evolved in the case of an irreversible heating, is higher than the thermal energy $\Delta U_1^{\prime 2}$ which is received by the system, but we don't explain the origin of the complementary energy defined as the difference between $T \Delta S_1^{\prime 2}$ and $\Delta U_1^{\prime 2}$. Here is the litigious point of the classical theory and as was seen when analyzing the previous example (the Joule experiment), the only possible solution for solving such conceptual problem is given by the Einstein mass-energy relation.

Since thermodynamic theory was known long before the mass-energy relation had been discovered, it was inconceivable for its authors to give the concept dU a larger signification than dU_e. Consequently, and while very powerful in practice, the thermodynamic tool they have invented is not perfectly coherent from a theoretical point of view. The usual concept of thermodynamics does not provide an explanation as to why relation (16) must be substituted by relation (18) in the case of real processes, nor in a more general way, as to why relation (4) must be substituted by relation (5).

To get around this difficulty, recent books of thermodynamics have often presented entropy in an axiomatic way. Entropy is defined as a state function whose variation dS is given by the relation:

$$dS \;=\; dS_e \;+\; dS_i \tag{23}$$

where
$$dS_e \;=\; dQ/T_e \tag{24}$$

dQ designating the thermal energy received (or given) by the system, and T_e the temperature of the surroundings. The reader is therefore informed, more or less abruptly, that the conditions are $dS_i = 0$ for a reversible process and $dS_i > 0$ for an irreversible process.

The undisputable efficiency of the thermodynamic tool is evidently linked to the fact that while not identified as such, the effect of the Einstein mass-energy relation is being taken into account. As will be shown below with numerical examples (part 5), it is implicitly present in equation (18) for

instance. Nevertheless, reconciling theoretical coherence with practical usefulness requires that the effect of the mass-energy relation is explicitly present in the equations.

B. New suggested interpretation

It is well known that combining (23) and (24) leads to the relation:

$$dS = dQ/T_e + dS_i \qquad (25)$$

which can be written indifferently:

$$T_e \, dS = dQ + Te \, dS_i \qquad (26)$$

Comparing equations (26) and (11) shows immediately their close analogy. Indeed, we obtain:

$$T_e \, dS = dQ + T_e \, dS_i \qquad (26)$$
$$dU^* = dU_e + dU_i \qquad (11)$$

Each term of equation (26) has the physical significance given by the corresponding term of equation (11), the one written on the same vertical. Referring to the heating process of a given mass of water as considered above, the detailed significance of the terms is the following:

o   The term dQ, equivalent to dU_e represents the thermal energy given to the system by the thermostat. Its value, as already seen, is the same whatever the level of irreversibility of the heating process.

o   The term $T_e \, dS_i$, equivalent to dU_i, represents the energy created inside the system by a partial disintegration of its mass, according to the Einstein mass-energy relation.

o   The term $T_e \, dS$ equivalent to dU^* represents the global energy which is involved in the heating process.

Note that the term dQ, intercalated between $T_e dS$ and $T_e dS_i$ in equation (26) has the signification $T_e dS_e$ as can be seen turning back to the definition of dS_e in equation (24). Concerning the system above, defined given mass of water that is evolving from state 1 (temperature T_1) to state 2 (temperature

T_2), by contact with a thermostat of temperature T_e, the integration of the three terms of relation (26) gives:

- For *TedS*:
$$\int_1^2 Te\ dS = Te \int_1^2 dS = Te\ C\ Ln\ \frac{T_2}{T_1} \qquad (27)$$

- For *dQ*:
$$\int_1^2 dQ = C\ (T_2 - T_1) \qquad (28)$$

- For *TedSi*:
$$\int_1^2 Te\ dSi = Te\ C\ Ln\ \frac{T_2}{T_1} - C\ (T_2 - T_1) \qquad (29)$$

In these relations, C is the heat capacity of the system (assumed constant over the integration interval). Noting the difference between C and c (the speed of light), the total integration of relation (26) gives:

$$T_e\ C\ Ln\ (T_2/T_1) = C\ (T_2 - T_1) + T_e\ \Delta S \qquad (30)$$

which means
$$T_e\ \Delta S = \Delta Q + T_e\ \Delta S_i \qquad (31)$$

or from (11)
$$\Delta U^* = \Delta U_e + \Delta U_i \qquad (32)$$

where
$$\Delta U_i = -c^2\ \Delta m \qquad (33)$$

Consequently
$$-c^2\ \Delta m = T_e\ C\ Ln\ (T_2/T_1) - C\ (T_2 - T_1) \qquad (34)$$

and
$$\Delta m = -c^{-2}\ T_e\ C\ Ln\ (T_2/T_1) - C\ (T_2 - T_1) \qquad (35).$$

All these theoretical considerations are summarized in an appendix at the end of the present paper. For a more concrete representation of their practical implications, some numerical examples will now be examined.

5. APPLICATIONS OF THE SUGGESTED THEORY TO NUMERICAL EXAMPLES

A. First example:

Let us return to the simple system defined as a given mass of water that receives heat by contact with a thermostat. We suppose that the initial conditions are:

- temperature of the water: *20 ° C (= 293 K)*

- temperature of the thermostat: *60 ° C (= 333 K)*

- mass of water: *0.24 g*, that gives for the thermal capacity *C = 1,* a value that will be considered constant over the temperature interval

Recalling that the dilatation of the system is negligible, the interpretation of the heating process presents some differences whether referring to the suggested theory or to the classical one. We obtain respectively:

With the suggested theory:

Calculating the two first terms of equation (30) gives:

$$T_e \, C \, Ln \, (T_2/T_1) \; = \; 333. \, 1. \, Ln(333/293)$$

$$= \; 333 \quad . \quad 0. \, 127 \, 969$$

$$= \; 42. \, 61 \; J$$

$$C \, (T_2 - T_1) \; = 1(\, 333 - 293) = 40 \, J$$

Consequently equations (30) to (34) lead to:

$$- c^2 \, \Delta \, m = T_e \, \Delta \, S \; - \; \Delta \, Q \; = 42. \, 61 \; - 40 \; = \; 2. \, 61 \; J$$

This last result *(2. 61 J)* represents the energy that is created inside the system, by a (very) partial disintegration of its mass according to the Einstein relation.

With the classical theory:

The successive steps of the calculation are:

$$\overset{\Delta}{} Q = 1(333 - 293) = 40 \ J$$

$$\Delta S = \int_{293}^{333} \frac{Cp}{T} \, dT = Ln \frac{333}{293} = 0.127\,969... \ J.\ K^{-1}$$

$$\Delta Se = \frac{\Delta Q}{Te} = \frac{40}{333} = 0.120\,120... \ J \ K^{-1}$$

$$\Delta S_i = \Delta S - \Delta S_e = 0.007\,848... \ J.\ K^{-1}$$

This last result is usually considered as outside the context of the Einstein mass-energy relation, but that is only an impression. As already emphasized, the "missing quantity" that represents the difference between $\overset{\Delta}{} Q$ and $T_e \overset{\Delta}{} S$ has the necessary dimensions of an energy. Thus, $\overset{\Delta}{} S_i$ must be multiplied by T_e, which leads to the energized quantity:

$$333 \ . \ 0.007\,848... = 2.61 \ J.$$

This result is the same as found earlier and represents the energy $T_e \overset{\Delta}{} S_i$ created inside the system, according to the theory of relativity.

B. Second example:

Let us consider an isolated system consisting of two parts, 1 and 2, that can exchange heat but not work. We suppose, for instance, that each of them is represented by a mass of water of *0.24 g* and that the initial temperatures are $T_1 = 293 \ K$ and $T_2 = 333 \ K$.

As can be observed experimentally (or obtained by thermodynamic calculation) the two temperatures will evolve toward a final value *313 K*. To calculate how much energy is created inside the system, we apply to part 1 and part 2 the previous procedure, which will give us:

For part 1:

$$\Delta U_1 = C_1 (313 - 293) = 20 \ J$$

$$\Delta S_1 = C_1 \ Ln \ (313/293) = 0.066 \ 030 \ J.K^{-1}$$

$$\Delta U_1 = T_1^* \ \Delta S_1$$

where T^*_1 (as already seen) is the mean temperature of part 1 during the process. Its value is $T^*_1 = \Delta U_1 / \Delta S_1 = 20/0.066 \ 030 = 302.89 \ K$.

For part 2:

Proceeding in a similar way gives us:

$$\Delta U_2 = -20 \ J, \quad \Delta S_2 = -0.061 \ 939 \ J.K^{-1} \quad T^*_2 = 322.89 \ K$$

For the whole system:

The term $T_e \ \Delta S$ has the following values:

For part 1: $T^*_2 \ \Delta S_1 = 322.89 \ . \ 0.066 \ 030 = +21.32 \ J$

For part 2: $T^*_1 \ \Delta S_2 = 302.89 \ . \ -0.061 \ 939 = -18.76 \ J$

Rewriting equations (31) and (32), we can note, just under them, the numerical values corresponding successively to part 1 and part 2. Then by adding the two contributions, we have the result concerning the whole system. This procedure yields:

$$T_e \, \Delta S \;=\; \Delta Q \;+\; T_e \, \Delta S_i \qquad (31)$$

$$\Delta U^* \;=\; \Delta U_e \;+\; \Delta U_i \qquad (32)$$

$$\text{part 1} \; : \quad 21.\,32 \;=\; 20 \;+\; 1.\,32$$

$$\text{part 2} \; : \quad -18.\,76 \;=\; -20 \;+\; 1.\,24$$

$$\text{Whole system} \; : \quad 2.\,56 \;=\; 0 \;+\; 2.\,56$$

This result can be condensed under the form:

$$\Delta U^* \;=\; \Delta U_e \;+\; \Delta U_i$$

$$2.\,56 \;=\; 0 \;+\; 2.\,56$$

The value $\Delta U_e = 0$ corresponds to the expression of the first law of thermodynamics in the case of an isolated system. In the classical concept, where the existence of ΔU_i is not recognized, it is simply written $\Delta U = 0$ as was done in the first pages of the present paper. The positive value of ΔU_i represents the energy which is created inside the system according to the theory of relativity.

Taking $c = 3.\,10^{\,8}\,ms^{-1}$, we obtain for the considered system:

$$\Delta m \;=\; -2.\,56 \,/(\,3.\,10^{\,8})^{\,2} \;=\; -2.\,84\,.\,10^{\,-17}\,kg$$

While not measurable in practice, this loss of mass appears as a necessary consequence of the suggested theory. As seen just above, the corresponding increase in energy is far from being negligible. Another interesting information lies in the fact that the energies which are created by loss of mass are positive for both part 1 and part 2, but their values are not the same. The value found for part 1 (whose initial temperature is the lowest) is higher than that created in part 2.

Returning to the previous example, if we consider that the water and the thermostat together constitute an isolated system, we can proceed as follows to calculate how much energy has been created

by disintegration of mass inside the thermostat.

According to the first law of thermodynamics, giving to the thermostat the symbol th, we can write $\Delta Ue_{th} = -40\ J$. We also have $T^*_{th} = 333\ K$, since the temperature of the thermostat can be considered constant in time and space. Then we can calculate ΔS_{th} using the relation $T^*_{th} = \Delta Ue_{th}/\Delta S_{th}$, giving $\Delta S_{th} = -40/333 = -0.120\ 120\ J.K^{-1}$. The next step consists in writing $T^*_e\,\Delta S_{th}$ where T^*_e is the mean temperature of the mass of water. Turning back to the vbalues already obtained, we find for the water, $T^*_e = \Delta U_e/\Delta S = 40/(0.127\ 969) = 312,57\ K$ and therefore $T_e\,\Delta S_{th} = -37.54\ J$. The energy created inside the thermostat is thus:

$$\Delta U^* \quad = \quad \Delta U_e \quad + \quad \Delta U_i$$

$$T_e\,\Delta S \quad = \quad \Delta Q \quad + \quad T_e\,\Delta S_i$$

$$-37.54 \quad = \quad -40 \quad + \quad 2.46$$

We see that the result is *2.46 J*, a value which is positive but less than that obtained for the water (*2.61 J*). While the initial mass of the thermostat is evidently much greater than that of the water, we note once again that the part of the system where the created energy is higher, is that with the lower initial temperature. Note that knowing the mass of the thermostat is not necessary for obtaining the value of the energy created inside it. Inversely, if the mass of the thermostat as well as that of water is known, the energy created in each part of the system can be expressed per unit of mass, emphasizing the difference between the value obtained for the water and that obtained for the thermostat.

6. CONCLUSION

We have suggested in this paper that to be solved, the conceptual difficulty of thermodynamics needs a synthesis of the classical laws of thermodynamics with the Einstein mass-energy relation. The main resulting idea is that the condition of evolution within a system, usually assimilated to an increase in entropy, should be extended to an increase in energy that is linked to a correlative decrease in mass. Far from being reserved to exceptional phenomena, the theory of relativity appears to be omnipresent around us.

In classical theory, as in our everyday life, an increase in energy is recognizable by a symptom such as an elevation of temperature for a supply of heat or a reduction in volume for a supply of work. What can be the concrete symptom of a decrease in mass, in the sense of the Einstein mass-energy relation?

Independently of the very indirect one that can be seen in the better coherence of the theory, the physical symptom of a decrease in mass is closely related to gravitation. The thermodynamic analysis

presented above has led to the conclusion that when two systems (or two parts of a system) exchange energy, the global result is an increase in energy, linked to a decrease in mass. According to Newton's general law of gravitation, it can be expected that the symptom of the decrease in mass is an extension of the distance separating the two systems. In the very local scale of the systems that were considered in part 5, the loss of mass is too small for having a visible effect, but integrating similar effects at the scale for two astronomical objects or systems, each of them undergoing internal irreversible processes, the reality of an extension of their mutual distance can be easily conceived. On that score, the idea of an expanding universe is in good accordance with the conclusions of the thermodynamic analysis presented here. We must have in mind however, that these conclusions concern what can be seen in our near part of the universe. It does not exclude the possibility that, in some other parts, the thermodynamic conditions of evolution could be reversed, implicating $dU_i < 0$ and $dm > 0$.

Acknowledgments

References :

[1] D. K. Nordstrom and J. L. Munoz, *Geochemical Thermodynamics,* Blackwell Scientific Publications 1986.

[2] G. M. Anderson and D. A. Crerar, *Thermodynamics in Geochemistry*, Oxford University Press, 1993.

Appendix (theoretical summary):

The main difference between the new suggested theory and the classical theory can be summarized as follows:

New suggested theory:

Reversible: $\delta Q + \delta W = dU_e = TdS - PdV$

Irreversible: $\delta Q + \delta W = dU_e = TdS - PdV$

so that $\delta Q + \delta W < dU_e + dU_i = TdS - PdV - c^2\, dm$

equivalent to $\delta Q + \delta W < dU_e + dU_i = T_e dS_e - PdV + T_e dS_i$

or $\delta Q + \delta W < dU^* = T_e dS - PdV$

Note that $T_e dS_e = TdS$; $T_e dS_i = -c^2\, dm$ and $T_e dS_e + TedS_i = TedS$

In the case of chemical or mineralogical reactions (which have not been examined in the present paper and implicate $dP = 0$ and $dT = 0$) the new suggested thermodynamic tool would take the form:

$$dG = -dUi = +c^2\, dm$$

where G is the Gibbs free energy of the considered system.

Classical theory:

Reversible: $\delta Q + \delta W = dU = TdS - PdV$

Irreversible: $\delta Q + \delta W = dU < TdS - PdV$

where dU has the signification dU_e and where the sign "<" means that dU_i is implicitly taken into account while not identified as such (which explains that the sign "<" is placed after dU, not before).

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