

An Instructive Difference between Theory and Practice in the Interpretation of the Second Law of Thermodynamics

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Abstract: In thermodynamics textbooks, the chapters dealing with the second law are logically located after those dealing with the first law. This implies that, in the presentation of the second law, the information obtained for the first law must be taken into account. In conventional thermodynamics this objective is bypassed rather than achieved because, as explained below, there is an instructive difference between theory and practice in the interpretation of the second law. Although the problem is simple, it needs the consideration of relativity - the Einstein mass-energy relation - to be solved.

Keywords: Thermodynamics, reversibility, irreversibility, energy, entropy, relativity, Einstein's mass-energy relation, relativity.

- 1 - A brief comeback on the first law of thermodynamics and its implications

Let us consider a thermodynamic system, defined as a gas contained in a cylinder equipped with a mobile piston. Admitting that this system can exchange heat and work with its surrounding, we focus attention on the basic equation classically written as:

$$dU = dQ + dW \quad (1)$$

where dQ represents the change in heat, dW the change in work and dU the change in internal energy of the system.

Depending on whether this energy exchange is reversible or irreversible, eq. 1 can be presented through the separate writings:

$$dU_{\text{rev}} = dQ_{\text{rev}} + dW_{\text{rev}} \quad (2)$$

$$dU_{\text{irr}} = dQ_{\text{irr}} + dW_{\text{irr}} \quad (3)$$

For a determined change of state of the system, the conventional understanding of the first law of thermodynamics lies in the potulate that we have the equality:

$$dU_{\text{irr}} = dU_{\text{rev}} \quad (4)$$

To simplify the discussion, let us suppose that the exchange of work between the system and its surrounding is limited to a work of volume. This is a way to say that dW_{irr} and dW_{rev} are totally defined by the relations:

$$dW_{\text{irr}} = - P_e dV \quad (5)$$

$$dW_{\text{rev}} = - P_i dV \quad (6)$$

where, referring to an elementary instant dt , P_e represents the external pressure (pressure of the surrounding) and P_i the internal pressure (pressure of the system)

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

$$dW_{irr} - dW_{rev} = dV(P_i - P_e) \quad (7)$$

Knowing that dV is positive when $P_i > P_e$ and negative when $P_i < P_e$, the product $dV(P_i - P_e)$ is always positive, so that we have in all cases:

$$dW_{irr} > dW_{rev} \quad (8)$$

Another possible writing of eq. 8 is therefore:

$$dW_{irr} = dW_{rev} + dW_{add} \quad (9)$$

where dW_{add} represents an additional energy, whose value is positive and whose existence is closely associated to the condition of irreversibility.

At this stage of the discussion, if we focus attention on the pair of equations 2, and 3 and remember that we have simultaneously $dU_{irr} = dU_{rev}$ (eq. 4) and $dW_{irr} > dW_{rev}$ (eq. 8), we easily conceive that the relation between the terms dQ_{irr} and dQ_{rev} is necessarily:

$$dQ_{irr} < dQ_{rev} \quad (10)$$

Consequently, the introduction of the second law must be done in such a way that the proposal given by eq. 10 should be respected. The problem is to see if it is really possible.

- 2 - Is it possible to introduce the second law in a way compatible with the first law?

In the same manner as we have encountered equations whose general form is $dW = - PdV$ in the presentation of the first law (eq. 5 and 6), it is well known that the second law is founded on equations whose general form is:

$$dQ = TdS \quad (11)$$

where T represents the absolute temperature, dS the change in entropy and dQ the heat exchanged by the system with its surrounding.

On the basis of this last equation, and remembering the procedure adopted for dW in eq. 5 and 6, the simplest idea that comes in mind is in imagining that the definitions of the terms dQ_{irr} and dQ_{rev} can be given by the respective equations:

$$dQ_{irr} = T_e dS \quad (12)$$

$$dQ_{rev} = T_i dS \quad (13)$$

The problem encountered with this approach lies in the fact that, for a given value of dS (which is the exact differential of the state function S , as well as dV is the exact differential of the state function V), the difference $dQ_{irr} - dQ_{rev}$ takes the form:

$$dQ_{\text{irr}} - dQ_{\text{rev}} = dS(T_e - T_i) \quad (14)$$

Observing (from eq. 11) that the sign of dS is always that of dQ (because T is necessarily positive, being an absolute temperature) we have $dS > 0$ if $T_e > T_i$ and $dS < 0$ if $T_e < T_i$.

For this reason, the product $dS(T_e - T_i)$ has always a positive value, leading to the general conclusion:

$$dQ_{\text{irr}} > dQ_{\text{rev}} \quad (15)$$

that can also be written:

$$dQ_{\text{irr}} = dQ_{\text{rev}} + dQ_{\text{add}} \quad (16)$$

where dQ_{add} represents an additional energy having a positive value, as was already the case of the term dW_{add} in eq. 9

Obviously, the result given by eq. 15 is not the expected one (eq. 10), but the opposite.

With the implicit hope that it will lead to the result $dQ_{\text{irr}} < dQ_{\text{rev}}$ the procedure generally adopted in textbooks consists in proposing that a reversible heat exchange between the system and its surrounding obeys the condition:

$$dS = dQ/T \quad (17)$$

while an irreversible heat exchange obeys the condition:

$$dS > dQ/T \quad (18)$$

When the reader is confronted to these propositions, his first reflex is to think that dQ means dQ_{rev} in eq. 17 and means dQ_{irr} in eq. 18. In such conditions, knowing that dS has the same value in both cases and supposing that the same condition could be true for T , he is led to the idea that dQ_{irr} and dQ_{rev} are linked by the relation $dQ_{\text{irr}} < dQ_{\text{rev}}$ as suggested by eq.10. At first glance, this indication seems to be the sign that the information derived from eq.17 and 18 is in perfect accordance with all the results already obtained concerning the first law.

In the passage from theory to practice - that is to the treatment of numerical examples - the situation gets less clear, because the reader discovers progressively that the precise meanings of eq. 17 and 18 are respectively:

Reversibility: $dS = dQ_{\text{rev}}/T_i \quad (19)$

that can also be noted:

$$dS = dQ_{\text{rev}}/T_e \quad (20)$$

(because the condition of reversibility implies $T_e = T_i$)

Irreversibility: $dS > dQ_{\text{rev}}/T_e \quad (21)$

equally written as:

$$dS = dQ_{\text{rev}}/T_e + dS_i \quad (22)$$

where the term dQ_{rev}/T_e is often designated under the symbol dS_e (external component of entropy) that refers to the heat exchange between the system and its surrounding, while dS_i (internal component of entropy) represents an additional entropy, interpreted as created inside the system.

To illustrate the fact that the procedure adopted in practice corresponds really to this series of equations, a numerical example - very simple - is given in appendix and commented.

Remaining in the theoretical debate, it can be observed through the precisions provided by the formulations just evoked that both terms dQ of eq. 17 and 18 represent dQ_{rev} , with the consequence that the relation between dQ_{irr} and dQ_{rev} cannot be extracted from a direct reading of these equations. A complementary step is needed whose first objective is precisely the derivation of the term dQ_{irr} from these equations. Since all the expressions 17 to 22 have the dimension of an entropy, it is interesting to transform the more detailed of them - that is eq. 22 - in an expression having the dimension of an energy.

The procedure consists in multiplying each term of eq. 22 by T_e and the result obtained is:

$$T_e dS = dQ_{\text{rev}} + T_e dS_i \quad (23)$$

whose meaning is:

$$dQ_{\text{irr}} = dQ_{\text{rev}} + T_e dS_i \quad (24)$$

Knowing that the term dS_i is always positive (fundamental information associated to the second law) and the term T_e too (absolute temperature), we see that the product $T_e dS_i$ is always positive.

Therefore, eq. 24 can be written under the form:

$$dQ_{\text{irr}} = dQ_{\text{rev}} + dQ_{\text{add}} \quad (25)$$

where dQ_{add} represents an additional energy having a positive value.

In such conditions, we see that the terms dQ_{irr} and dQ_{rev} are linked together by the relation:

$$dQ_{\text{irr}} > dQ_{\text{rev}} \quad (26)$$

This last result is nothing but the proposition given above by eq. 15 which was directly derived from the hypothesis that eq. 12 and 13 can be adequate definitions of dQ_{irr} and dQ_{rev} . This is the sign that when we use eq. 17 and 18 as a starting basis for the presentation of the second law of thermodynamics, the idea that they are compatible with the expected result $dQ_{\text{irr}} < dQ_{\text{rev}}$ (eq. 10) is just an impression. The reality is that the information hidden behind eq. 17 and 18 corresponds itself to the proposition $dQ_{\text{irr}} > dQ_{\text{rev}}$.

- 3 - Consequences of the results already obtained.

Having noted that the inequality $dQ_{\text{irr}} > dQ_{\text{rev}}$ can be derived indifferently from the entropy equations 17 and 18 or from the energy equations 12 and 13, we have the choice between both starting basis. It seems that the pair of eq. 12 and 13 constitutes a better choice, because it leads directly to the inequality $dQ_{\text{irr}} > dQ_{\text{rev}}$ and represents a procedure more homogeneous with the one adopted for the terms dW_{irr} and dW_{rev} . Indeed, eq. 12 and 13 that concern dQ are very similar to eq. 5 and 6 that concern dW , as well as eq. 25 is very similar to eq. 9.

The main consequence of the inequality $dQ_{\text{irr}} > dQ_{\text{rev}}$ is evidently that, being associated to the inequality $dW_{\text{irr}} > dW_{\text{rev}}$ (eq. 8), it implies that the equality $dU_{\text{irr}} = dU_{\text{rev}}$, classically understood as the adequate formulation of the first law of thermodynamics, needs to be substituted by the inequality:

$$dU_{\text{irr}} > dU_{\text{rev}} \quad (27)$$

that can also be written:

$$dU_{\text{irr}} = dU_{\text{rev}} + dU_{\text{add}} \quad (28)$$

where dU_{add} represents an additional energy having a positive value.

As suggested in previous papers [1, 2], the origin of this additional energy seems to be linked to the Einstein mass-energy relation $E = mc^2$. It is a way to say that every irreversible process generates - inside the system to which it refers - an energy due to a correlative disintegration of matter. Although the change in mass, in most cases, is too small to be detectable, the corresponding increase in energy appears as a general feature, giving to the term dU_{add} the significance:

$$dU_{\text{add}} = -c^2 dm \quad (29)$$

and to eq. 28 the significance:

$$dU_{\text{irr}} = dU_{\text{rev}} - c^2 dm \quad (30)$$

In eq. 29 and 30, the minus sign placed in front of the term $c^2 dm$ appears as a necessary condition to give $dU_{\text{add.syst}}$ a positive value. The procedure is the same as that used in eq. 5 to give dW a positive value when the system receives work (i.e. when the volume obeys the condition $dV < 0$) and a negative value when it provides work (i.e. when the volume obeys the condition $dV > 0$).

It is interesting to note that in recent textbooks [3, 4], the need to connect thermodynamics with relativity is evoked.

- 3 – Conclusion

As a result of this discussion, the important point to keep in mind is that the adequate understanding of the first law is not given by the proposition $dU_{\text{irr}} = dU_{\text{rev}}$, but by the proposition $dU_{\text{irr}} = dU_{\text{rev}} + dU_{\text{add}}$ (eq. 27), even when the starting basis adopted for the presentation of the second law corresponds to the pair of equations 17 and 18.

In such conditions, it seems that there is no reason to maintain the habit of using the entropy equations 17 and 18 in the presentation of the second law. The choice of energy equations 12 and 13 is simpler because, associated to eq. 5 and 6 that refer to dW , they lead more directly to eq. 27.

Far from being a drawback, this substitution can be felt as an advantage, since it eliminates the conceptual difficulties we are facing, when we try to be convinced that eq. 17 and 18 are compatible with the proposition $dQ_{\text{irr}} < dQ_{\text{rev}}$ (eq. 10). As explained above, this compatibility does not exist, since the result derived from the entropy equations 17 and 18 is $dQ_{\text{irr}} > dQ_{\text{rev}}$ (eq. 26), the same as that derived from the energy equations 12 and 13 (eq. 15). The fundamental reason of this situation lies in the positive value of the internal component of entropy ($dS_i > 0$), evidenced a long time ago by the pionniers of thermodynamics.

If they agree with this conception, it seems that professors of physics and chemistry might try to test it in their courses, knowing that it is not a rejection of the conventional theory but an extension. It consists in the idea that the internal increase in entropy (positive value of the term dS_i in eq. 22) is the symptom of an internal increase in energy (positive value of the term $T_e dS_i$ in eq. 24, and therefore of the term dQ_{add} in eq. 25)

Eq. 29 is a preliminary hypothesis suggesting a connection between this additional energy and the Einstein mass-energy relation. Similarly, eq. 30 is a preliminary attempt to collect the first law, the second law and the mass-energy relation in a single formulation.

- 4 – References

- [1] J-L. Tane, *Thermodynamics and Relativity: A Condensed Explanation of their Close Link*. <http://arxiv.org/pdf/physics/0503106> 2005
- [2] J-L Tane, *Unless connected to Relativity, the First and Second Laws of Thermodynamics are Incompatible*. The General Science Journal and <http://arxiv.org/abs/0910.0781> 2010
- [3] D. Kondepudi, *Introduction to Modern Thermodynamics* Wiley 2008 (see p. 79-80, the comment on the thermodynamic interpretation of nuclear reactions)
- [4] B. Linder, *Elementary Physical Chemistry* World Scientific 2011 (see p. 15, the wish to insert the mass-energy relation in the first law)

Appendix

Destined to illustrate what has been said in the passage from eq. 17 to eq. 22, the numerical example chosen below is extracted from a thermodynamics course. It consists in calculating the change in entropy (ΔS , ΔS_e and ΔS_i) of 1 liter of water (1000 g) that is heated from 20° C (293 K) to 100° C (373 K), by contact with a thermostat at 100° C (373 K).

Knowing that $c_{p_{\text{water}}} = 4,18 \text{ J g}^{-1}$ and admitting that it can be considered constant over the interval of temperature, the answer is detailed as follows:

$$\Delta S = \int_{293}^{373} \frac{dQ}{T} = m c_p \int_{293}^{373} \frac{dT}{T} = 1000 \times 4,18 \times \ln 373/293 = 1009 \text{ J.K}^{-1} \quad (\text{A})$$

$$\Delta S_e = \Delta Q/T_e = [1000 \times 4,18 (373 - 293)] / 373 = 334\,400/373 = 896 \text{ J.K}^{-1} \quad (\text{B})$$

$$\Delta S_i = \Delta S - \Delta S_e = 1009 - 896 = 113 \text{ J.K}^{-1} \quad (\text{C})$$

If we compare these equations with those encountered in section 2 (eq. 17 to 22) we have the following correspondances:

In eq. B, the term $\Delta Q = [1000 \times 4,18 \times (373 - 293)] = 334\,400$ represents ΔQ_{rev} , that is the integration of the term dQ_{rev} of eq. 21 and 22. The detailed expression is:

$$\Delta Q_{\text{rev}} = mcp \int_{293}^{373} dT = 1000 \times 4,18 (373 - 293) = 334\,400 \text{ J}$$

In eq. A, the term $mcp \int_{293}^{373} \frac{dT}{T}$ can also be noted:

$$\frac{1}{T^*} mcp \int_{293}^{373} dT = \frac{1}{T^*} [1000 \times 4,18 \times (373-293)] = \frac{\Delta Q_{\text{rev}}}{T^*}$$

where T^* is the average temperature T during the heating process. Knowing that in conditions of reversibility, we have always $T_e = T_i$, the symbol T^* represents indifferently T_i^* and T_e^* .

Having $\Delta S = 1009 \text{ J.K}^{-1}$ and $\Delta Q_{\text{rev}} = 334\,400 \text{ J}$, the value of T^* is:

$$T^* = \Delta Q_{\text{rev}} / \Delta S = 334\,400 / 1009 = 331 \text{ K}$$

As already noted in paragraph 2, the term ΔQ_{irr} is not directly visible in these equations, but using the results just obtained and integrating eq. 12 and 13, we get respectively:

$$\Delta Q_{\text{irr}} = T_e \Delta S = 373 \times 1009 = 376\,357 \text{ J}$$

$$\Delta Q_{\text{rev}} = T_i^* \Delta S = 331 \times 1009 = 333\,979 \text{ J}$$

The slight difference (0,12 %) between this last result (333 979 J) and the one previously found for ΔQ_{rev} (334 400 J) comes from the fact that the indication $T^* = 331 \text{ K}$ is a rounded value.

Then using eq. 24, the term ΔQ_{add} can be calculated by difference. Its value is:

$$\Delta Q_{\text{add}} = \Delta Q_{\text{irr}} - \Delta Q_{\text{rev}} = 42378 \text{ J}$$

It can be seen through these results that we have really $\Delta Q_{\text{irr}} > \Delta Q_{\text{rev}}$ and that the positive difference ΔQ_{add} represents an additional energy that is created inside the system, linked to the fact that the heating is performed under conditions of irreversibility ($T_e \neq T_i$).