A Simplified Interpretation of the Basic Thermodynamic Equations

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Abstract: In the discussion presented below, the basic equations used to describe heat exchanges are similar to those used to describe work exchanges. It is shown that the information they lead to is equivalent to the one given by the conventional approach. The only - but fundamental - difference is that the concept of increase in entropy appears as the symptom of an increase in energy, implying a link between thermodynamics and relativity. With the help of a numerical example, the difference between the classical theory and the new suggested interpretation is analyzed in detail.

Keywords: Thermodynamics, reversibility, irreversibility, energy, entropy, relativity, Einstein’s relation

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- 1 - Brief recall of the matter already exposed

1.1. The concepts of reversibility and irreversibility

a) Work exchange. When a thermodynamic system is concerned by a mechanical work exchange, the equation corresponding to the general case of an irreversible process is:

\[ dW_{irr} = -P_e \, dV \]  \hspace{1cm} (1)

where \( dV \) represents the volume change, \( P_e \) the external pressure and \( dW \) the change in work.

In the case of a reversible process, eq. 1 becomes:

\[ dW_{rev} = -P_i \, dV \]  \hspace{1cm} (2)

where \( P_i \) represents the internal pressure.

Therefore the difference \( dW_{irr} - dW_{rev} \) can be written through the relation:

\[ dW_{irr} = dW_{rev} + dV(P_i - P_e) \]  \hspace{1cm} (3)

Since \( dV \) is positive when \( P_i > P_e \) and negative when \( P_i < P_e \), the term \( dV(P_e - P_i) \) is always positive, and we get in all conditions the relation:

\[ dW_{irr} > dW_{rev} \]  \hspace{1cm} (4)

b) Heat exchange. Let us imagine that similarly to the exchange of work just examined (eq. 1 and 2), the basic equations describing an exchange of heat could be written:

\[ dQ_{irr} = T_e \, dS \]  \hspace{1cm} (5)
\[ dQ_{\text{rev}} = T_i \, dS \]  

(6)

The function \( S \), called entropy, being a state function, \( dS \) has the same value whatever is the level of irreversibility of the heating process, and the difference \( dQ_{\text{irr}} - dQ_{\text{rev}} \) takes the form:

\[ dQ_{\text{irr}} - dQ_{\text{rev}} = dS(T_e - T_i) \]  

(7)

The terms \( T_e \) and \( T_i \) being positive (absolute temperatures), eq. 5 and 6 imply that the sign of \( dS \) is always that of \( dQ \) (which is evidently the same for \( dQ_{\text{irr}} \) and \( dQ_{\text{rev}} \)).

Having \( dQ > 0 \) when \( T_e > T_i \) and \( dQ < 0 \) when \( T_e < T_i \), the same is true for \( dS \). Therefore, the term \( dS(T_e - T_i) \) is always positive and implies the relation:

\[ dQ_{\text{irr}} > dQ_{\text{rev}} \]  

(8)

c) **First general conclusion**

The function \( U \), called "internal energy", being defined by the relation:

\[ dU = dQ + dW + \ldots. \]  

(9)

the considerations just evoked imply the relation:

\[ dU_{\text{irr}} > dU_{\text{rev}} \]  

(10)

Consequently, if an isolated system is made of several parts having mutual exchanges of energy, applying eq. 10 to the different parts leads to the relation:

\[ dU_{\text{irr}, \text{syst}} > dU_{\text{rev}, \text{syst}} \]  

(11)

where \( dU_{\text{syst}} \) represents the change in energy of the whole system.

Taking into account that \( dU_{\text{rev}, \text{syst}} = 0 \) and that a real process is always irreversible, this proposition means that when an isolated system is concerned by internal exchanges of energy, its own energy increases.

**1.2. Preliminary comparison with the conventional theory**

In conventional thermodynamics, the first law consists of admitting as a fundamental postulate the relation:

\[ dU_{\text{irr}} = dU_{\text{rev}} \]  

(12)

Correlatively, the second law is classically understood through the relation:

\[ dS = dQ/T + dS_i \]  

(13)

whose precise meaning is:

\[ dS = dQ_{\text{rev}} / T_e + dS_i \]  

(14)
Obviously, this conception is different from the one considered above, that gives to the first law the understanding summarized through eq. 11

Correlatively, it can be seen that, from the mathematical point of view, eq. 14 can be presented under the form:

\[ T_e \, dS = dQ_{\text{rev}} + T_e \, dS_i \]  \hspace{1cm} (15)

whose significance is:

\[ dQ_{\text{irr}} = dQ_{\text{rev}} + T_e \, dS_i \] \hspace{1cm} (16)

Knowing that \(dS_i\) is a positive term (fundamental information linked to the second law) and \(T_e\) too (absolute temperature), the term \(T_e \, dS_i\) is positive, so that eq. 14, 15 and 16 appear consistent with eq. 7. Their comparison implies the equality:

\[ dS(T_e - T_i) = T_e \, dS_i \] \hspace{1cm} (17)

It can be noted that, from the physical point of view too, eq. 14 and 15 are closely connected with one another, since eq. 15 is nothing but the transcription, in terms of energy, of the information given by eq. 14 in terms of entropy.

Taking into account this remark and observing that both eq. 4 and 8 are particular cases of eq. 10, the idea has been suggested in previous papers [(1), (2), (3)] to extend the interpretation of the thermodynamic theory. The extension consists of combining the first law and second law in the single formula:

\[ dU_{\text{irr}} = dU_{\text{rev}} + dU_{\text{add}} \] \hspace{1cm} (18)

where \(dU_{\text{add}}\), represents an additional energy having a positive value.

Concerning the origin of this additional energy, it seems that the Einstein mass-energy relation \(E = mc^2\) offers the simplest possible explanation. This is the reason why, in the papers just evoked, the term \(dU_{\text{add}}\) is substituted by the differential - \(c^2 dm\), giving to eq. 18 the formulation:

\[ dU_{\text{irr}} = dU_{\text{rev}} - c^2 dm \] \hspace{1cm} (19)

The minus sign placed in front of the term \(c^2 dm\) expresses the idea that an increase in energy could be linked to a decrease in mass

As will be seen below, this interpretation brings some interesting simplifications.

The existence of a link between thermodynamics and relativity has been pointed out and analyzed for a long time [4]. In the recent years, several articles on the subject have been published [(5), (6), (7), (8)].
2.1 An important remark concerning their integration

Let us consider a system defined as a gas contained in a cylindrical vessel, equipped with a mobile frictionless piston. If its volume varies from a value $V_1$ to a value $V_2$, the corresponding change in work, calculated by integration of eq. 1 takes the form:

$$\Delta W_{\text{irr}} = \int_{V_1}^{V_2} -P_e \, dV$$

(20)

If $P_e$ is constant, eq. 20 can be written:

$$\Delta W_{\text{irr}} = -P_e \left[ \Delta V \right]_{V_1}^{V_2}$$

(21)

If $P_e$ is not constant, it can be written:

$$\Delta W_{\text{irr}} = -P_e^* \left[ \Delta V \right]_{V_1}^{V_2}$$

(22)

where $P_e^*$ is the average value of $P_e$ during the process.

For a given process, the term $P_e^*$ represents a mathematical constant, with the important consequence that, in such conditions, we have necessarily:

$$dP_e^* = 0$$

(23)

In a similar way, the integration of eq. 5 leads to:

$$\Delta Q_{\text{irr}} = \int_{S_i}^{S_2} T_e \, dS$$

(24)

If $T_e$ is constant, eq. 24 can be written:

$$\Delta Q_{\text{irr}} = T_e \left[ \Delta S \right]_{S_i}^{S_2}$$

(25)

If $T_e$ is not constant, eq. 23 becomes:

$$\Delta Q_{\text{irr}} = T_e^* \left[ \Delta S \right]_{S_i}^{S_2}$$

(26)

where $T_e^*$ is the average value of $T_e$ during the process, and implies the condition:

$$dT_e^* = 0$$

(27)
The same situation is true for $T_i$ and $P_i$ in the sense that their general significance can be noted $T_i^*$ and $P_i^*$, and obeys the relations:

\begin{align}
    dT_i^* &= 0 \\
    dP_i^* &= 0
\end{align}

2.2 Detailed formulations of the terms $dU_{irr}$, $dU_{rev}$, and $dU_{add}$

It results from the considerations examined above that the terms $dU_{irr}$, $dU_{rev}$ and $dU_{add}$ can be defined as:

\begin{align}
    dU_{irr} &= dW_{irr} + dQ_{irr} \\
    dU_{rev} &= dW_{rev} + dQ_{rev} \\
    dU_{add} &= dU_{irr} - dU_{rev} = -c^2dm
\end{align}

Taking in account that, in thermodynamic language, the form $TdS - PdV$ is more familiar than the form $-PdV + TdS$, the detailed formulation of eq. 30, 31 and 32 can be written:

\begin{align}
    dU_{irr} &= T_e^*dS - P_e^*dV \\
    dU_{rev} &= T_i^*dS - P_i^*dV \\
    dU_{add} &= (T_e^*dS - P_e^*dV) - (T_i^*dS - P_i^*dV) = -c^2dm
\end{align}

Therefore, another writing for $dU_{rev}$ is:

\begin{align}
    dU_{rev} &= (T_e^*dS - P_e^*dV) + c^2dm
\end{align}

Concerning $dW$ and $dQ$, it becomes always to possible write:

\begin{align}
    dW_{irr} &= -P_e^*dV \\
    dQ_{irr} &= T_e^*dS
\end{align}

This last couple of equations differs from the classical conception, where eq. 37 is admitted, but not eq. 38.

2.3 Illustration of the use of these equations through a numerical example

Let us consider the very simple case of a given mass of water that is heated a constant pressure (the atmospheric pressure) by contact with a thermostat at temperature $T = 313$ K. We suppose that its heat capacity is $C = 1000$ J, that corresponds to a mass of 239 g, since the specific heat capacity of water is $c = 4,18$ JK$^{-1}$ g$^{-1}$.

Admitting that the temperature of the water varies from $T_1 = 293$ K (initial state) to $T_2 = 313$ K (final state), the difference between the classical interpretation of the process and the new
suggested one is summarized below. The question is discussed with successive references to three thermodynamic functions: the internal energy (U), the enthalpy (H), the free energy (G). The function entropy (S) is concerned with the all parts of the discussion.

2.3.1 Analysis of the process through the function internal energy U

a) Classical interpretation

The function U is introduced in its differential form, that is:

\[ dU = dQ + dW = dQ - PdV \]  \hspace{1cm} (39)

Although not always written, it is implicitly understood that P means \( P_e \). When the system evolves from state 1 to state 2, the dilation of the water (not very important in the present case) can be taken into account by the integration of the term - PdV. Since V is a state function, and \( P_e \) a constant, the term - PdV is an exact differential. This is equally the case of dU, (classical conception of the first law). Therefore dQ is seen as an exact differential too.

The numerical value \( \Delta Q \) is calculated by integration of the equation:

\[ dQ = mc dT \]  \hspace{1cm} (40)

Having here \( mc = 1000 \text{JK}^{-1} \), the result obtained is \( \Delta Q = 1000 \times (313 - 293) = 20000 \text{J} \). It is considered as representing indifferently \( \Delta Q_{\text{rev}} \) and \( \Delta Q_{\text{irr}} \).

As concerns the calculation of S, the starting equation is

\[ dS = \frac{C_p}{T} dT \]  \hspace{1cm} (41)

Taking into account that, for the liquid water, the value \( C = 4.18 \text{JK}^{-1} \) is valid for both \( C_p \) and \( C_v \), and can be assumed constant between \( T_1 \) and \( T_2 \), the result obtained is:

\[ \Delta S = 1000 \text{Ln}(313/293) = 66.030 \text{JK}^{-1} \]  \hspace{1cm} (42)

Since the heating has been done by contact with a thermostat at \( T = 313 \text{K} \), it can be specified that:

\[ \Delta S_e = \Delta Q/T_e = 20000/313 = 63.898 \text{JK}^{-1} \]  \hspace{1cm} (43)

and that:

\[ \Delta S_i = \Delta S - \Delta S_e = 2.132 \text{JK}^{-1} \]  \hspace{1cm} (44)

b) New suggested interpretation

The equality \( dU_{\text{irr}} = dU_{\text{rev}} \) being substituted by relation \( dU_{\text{irr}} > dU_{\text{rev}} \), we have to calculate separately the terms \( \Delta Q_{\text{rev}} \) and \( \Delta Q_{\text{irr}} \).

Concerning \( \Delta Q_{\text{rev}} \), the value is the one found above, i.e. \( \Delta Q_{\text{rev}} = 20000 \text{J} \).
Concerning $\Delta Q_{irr}$, the calculation is done by integration of eq. 15, whose expression is:

$$T_e \, dS = dQ_{\text{rev}} + T_e \, dS_i$$

Since $T_e = \text{constant} = 313$ K, we get:

$$T_e \, \Delta S = \Delta Q_{\text{rev}} + T_e \, \Delta S_i \quad (44)$$

whose meaning is

$$\Delta Q_{irr} = \Delta Q_{\text{rev}} + \Delta Q_{\text{add}} \quad (45)$$

that is

$$\Delta Q_{irr} = \Delta Q_{\text{rev}} - c^2 \Delta m \quad (46)$$

Having $\Delta S = 66.030 \, \text{JK}^{-1}$ (result found above), we get $\Delta Q_{irr} = T_e \, \Delta S = 20\,667.39 \, \text{J}$

By difference

$$\Delta Q_{\text{add}} = T_e \, \Delta S_i = 667.39 \, \text{J} \quad (47)$$

Therefore $\Delta m = -667.39 / [(3 \times 10^8)^2] = 7.45 \times 10^{-15} \, \text{kg} \quad (48)$

Although this change in mass is too small to be detectable experimentally, it appears as a fundamental data from the theoretical point of view.

### 2.3.2 Analysis of the process through the function enthalpy $H$

#### a) Classical interpretation

The state function $H$ being defined as $H = U + PV$, its differential is:

$$dH = dU + PdV + VdP \quad (49)$$

In the classical interpretation, this equation is understood as having the significance:

$$dH = dU + P_e dV + VdP_e$$

with $dU = dQ + dW = dQ - P_e dV$,

Therefore

$$dH = dQ - P_e dV + P_e dV + VdP_e \quad (50)$$

which reduces to

$$dH = dQ + VdP_e \quad (51)$$

Having $dP_e = 0$ (since $P_e = \text{constant}$)

we get $dH = dQ$

Therefore $\Delta H = \Delta Q = 20\,000 \, \text{J}$ (result obtained above in section 2.3.1.a) \quad (52)

#### b) New suggested interpretation
As will be seen below, the value found for $\Delta H$ is the same, but not the interpretation. The reason comes from the fact that contrary to the classical approach, where the term $dU$ of eq. 49 means $dU = dQ - P_e dV$, it is understood here as being $dU_{rev}$ and therefore cannot contain a component of the form $P_e dV$.

In other words, eq. 49 has the significance:

$$dH = dU_{rev} + P_e^* dV + VdP_e^*$$

that is:

$$dH = (T_i^* dS - P_i^* dV) + P_e^* dV + VdP_e^*$$

that can equally be written:

$$dH = T_i^* dS + (P_e^* - P_i^*) dV + VdP_e^*$$

This Eq. 55 presents the following peculiarities:

The difference $(P_e^* - P_i^*)$ being negligible in the context presently examined, we can consider as an acceptable approximation the equality $(P_e^* - P_i^*) dV = 0$. This allows to eliminate the terms of the form $PdV$, as in the previous case, but not for the same reasons.

The value $VdP_e^*$ is equally zero, not only because we are in a particular case where $P_e$ is constant, but because we have seen with eq. 23 that the condition $dP_e^* = 0$ is general. It remains true even when the external pressure $P_e$ is variable

As a consequence, $dH$ reduces to

$$dH = T_i^* dS$$

whose integration gives:

$$\Delta H = T_i^* \Delta S$$

The term $T_i^*$ can be calculated by eq. 25 whose expression is

$$\Delta Q_{irr} = T_e^* [\Delta S]_{S_1}^{S_2}$$

In conditions of reversibility (limited case of an irreversibility), this equation becomes:

$$\Delta Q_{rev} = T_i^* [\Delta S]_{S_1}^{S_2}$$

so that

$$T_i^* = \Delta Q_{rev}/\Delta S = 20 000 / 66.030 = 302.89 K$$

Then, from eq 57, we get: $\Delta H = 302.89 \times 66.030 = 20 000 J$

NB: In the calculation just presented, the concept of change in mass does not appear. To make it visible, the term $dU_{rev}$ of eq. 53 must be written in the form given by 36. In doing so, eq. 53 becomes:
\[ dH = T_c^* dS - P_c^* dV + c^2 dm + P_c^* dV + VdP_c^* \]  \hspace{1cm} (60)

After simplification, and since \( dp_c^* = 0 \), the integrated form of this expression reduces to:

\[ \Delta H = T_c^* \Delta S + c^2 \Delta m \]  \hspace{1cm} (61)

Having \( \Delta H = 20\,000 \text{ J} \) and \( T_c^* \Delta S = 313 \times 66.030 = 20\,667.39 \text{ J} \), we get \( c^2 \Delta m = -667.39 \text{ J} \).

This result is the same as the one found above. It implies \( \Delta m = -7.45 \times 10^{-15} \text{ kg} \).

2.3.3 Analysis of the process through the function free energy \( G \)

Although it not of common use to analyze with the help of the function \( G \) a process as simple as the heating of a sample of water, the test brings some interesting information.

a) Classical interpretation

The function free energy \( G \), is defined by the relation:

\[ G = H - TS \]  \hspace{1cm} (62)

Its differential is:

\[ dG = dH - T_e dS - SdT \]  \hspace{1cm} (63)

whose meaning is:

\[ dG = dH - T_c dS - SdT \]  \hspace{1cm} (64)

Having in the present case \( dT_c = 0 \) (since the heat source is a thermostat), eq. 64 reduces to:

\[ dG = dH - T_c dS \]  \hspace{1cm} (65)

Due to the constancy of \( T_c \), the integrated form of eq. 65 can be written:

\[ \Delta G = \Delta H - T_c \Delta S \]  \hspace{1cm} (66)

Then entering in eq. 66 the numerical values already noted (\( T_e = 313 \text{ K} \), \( \Delta H = 20\,000 \text{ J} \) and \( \Delta S = 66.030 \text{ JK}^{-1} \)), we get \( \Delta G = -667.39 \text{ J} \).

b) New suggested interpretation

The precise meaning of eq. 64 is:

\[ dG = dH - T_c^* dS - SdT_c^* \]  \hspace{1cm} (67)

Entering in eq. 67 the expression of \( dH \) given by eq. 53, we get:
\[ dG = dU_{rev} + P_c^*dV + VdP_c^* - T_c^*dS - SdT_c^* \]  

(68)

Entering in eq. 68 the expression of \( dU_{rev} \) given by eq. 34, leads to:

\[ dG = T_i^*dS - P_i^*dV + P_c^*dV + VdP_c^* - T_c^*dS - SdT_c^* \]  

(69)

Then knowing from eq. 23 and eq. 27 that \( dP_c^* = 0 \) and \( dT_c^* = 0 \), we see that eq. 69 can be written:

\[ dG = dS ( T_i^* - T_c^*) + dV (P_c^* - P_i^*) \]  

(70)

If we assume the equality \( P_i = P_e \) (since the water is heated at constant pressure), we get:

\[ dG = dS ( T_i^* - T_c^*) \]  

(71)

whose integrated form is:

\[ \Delta G = \Delta S ( T_i^* - T_c^*) \]  

(72)

Having noted above that \( \Delta S = 66.030 \text{ JK}^{-1} \), \( T_i^* = 302.89 \text{ K} \) and \( T_c^* = 313 \text{ K} \), the result obtained is \( \Delta G = -667.56 \text{ J} \). It confirms the one previously found.

As already seen with eq. 48, the correlative change in mass is \( \Delta m = 7.45 \times 10^{-15} \text{ kg} \).

c) Complementary remark

Due the fact that the result \( \Delta G = -667.56 \text{ J} \) found above is in good agreement with the value \( \Delta G = -667.39 \text{ J} \) given by the usual approach, we can be tempted to conclude that this last one is perfectly consistent, without requiring the need of an additional energy.

Such an impression is not always true: Remaining in the context and language of the classical conception, imagine that instead of writing \( G \) in the form \( G = H - TS \), we write it in the form:

\[ G = U + PV - TS \]  

(73)

In such a case, the differential becomes:

\[ dG = dU + PdV + VdP - TdS - SdT \]  

(74)

Giving to \( dU \) the significance \( dU = TdS - PdV \) (as generally done for simple thermo-mechanical processes in the classical conception) eq. 74, after simplifications, reduces to:

\[ dG = VdP - SdT \]  

(75)

Then observing that \( dP = 0 \) and \( dT = 0 \) (since \( P \) means \( P_e \) and \( T \) means \( T_e \) which both are constant in the present context) the conclusion we are led to takes the form:
This result disagrees not only with the one just above obtained, but equally with the one found by the classical theory when the starting formula is \( G = H - TS \).

In such a situation, the need is sometimes felt to insert in eq. 74 a complementary detail in order to obtain for \( \Delta G \) a value which is not zero. Another possible issue is to decide that the function \( G \) is reserved for the processes including chemical reactions. Indeed, in this last context, the complementary element is given by the terms of the form \( \mu d\mu \), referring to the chemical potentials.

It seems that the alternative interpretation suggested above provides a more general answer.

d) An important property of the function free energy \( G \)

If the term \( dU_{\text{rev}} \) inserted in eq. 68 is the one given by eq. 36, the differential obtained for \( dG \) takes the form:

\[
dG = (T_c^* dS - P_c^* dV + c^2 dm) + P_c^* dV + V dP_c^* - T_c^* dS - S dT_c^*
\]  

(77)

After simplifications, and taking into account that \( dP_c^* \) and \( dT_c^* \) are zero, eq. 77 reduces to:

\[
dG = + c^2 dm
\]  

(78)

Confronted with eq. 30, 31 and 32, eq. 78 shows that \( dG \) obeys the relation:

\[
dG = - dU_{\text{add}} = dU_{\text{rev}} - dU_{\text{irr}} = + c^2 dm
\]  

(79)

This relation is an important property of the function \( G \). It is the sign that for a given process, the term \( - \Delta G \) represents the energy \( \Delta U_{\text{add}} \) that is created by disintegration of mass (\( \Delta m < 0 \)).

As mentioned in a previous papers [3], this proposition concerns inert systems (i.e. the systems made of inert matter). It is not excluded that living systems evolve in the opposite direction, with \( \Delta G \) representing the energy that is regenerated in matter (\( \Delta m > 0 \)).

- 3 - Conclusions

Due to the fact that it appears very simple, the hypothesis presented in this paper asks an evident question: how can we explain that it has not been inserted into the thermodynamic theory at the time of its creation?

There are probably two reasons to explain this situation.

The first one is that the Einstein mass-energy relation, which gives the basis of this alternative hypothesis, was not known at that time.

The second is that the practical efficiency of the thermodynamic tool being unquestionable, it does not call suspicions about the consistency of the theory.
What is sure is that the understanding of thermodynamics is known to be difficult. Even authors of textbooks have evoked the problem, giving their impression that something is not totally clear in the subject [(9), (10)]. It seems that, connected with relativity, the thermodynamic theory becomes simpler.

- 4 - References


