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THE DIFFICULTY OF ATTRIBUTING A PHYSICAL SIGNIFICANCE TO QUANTITIES WORK AND HEAT IN THE FIRST PRINCIPLE OF THERMODYNAMICS. THE RESOLUTION OF AN ENTROPY MAXIMIZATION CONTROVERSY *

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RESUMO

Escolheram-se dois processos para evidenciar a dificuldade em atribuir significado físico à primeira Lei da Termodinâmica - $dU=dW+dQ$, dado não ser possível separar a troca energética entre dois subsistemas, dividindo-a em trabalho - dW, e calor - dQ, com significado energético (atribuído a cada um destes termos), mesmo que se admita que a transformação é *"quasi-estática"*. Através da análise destes processos mostramos que a Primeira Lei não possui o significado que habitualmente se lhe atribui. A análise que se apresenta completa a recentemente publicada [3].

ABSTRACT

Two processes have been chosen to show the difficulty of attributing a physical significance to the first law - $dU=dW+dQ$, since it is not possible to separate the energetic exchange between two subsystems, dividing it into work - dW, and heat - dQ, with an energetic significance (attributed to each one of these terms), even if an *"quasi-static"* transformation is assumed. By analysing these processes we have show that the First Law does not possess the significance commonly attributed to it. The analysis developed herein completes one recently published [3].

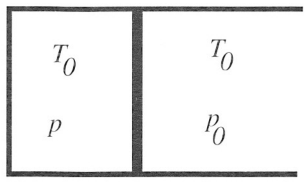
INTRODUCTION

The First Law of Thermodynamics led to a conceptual revision of the significance of work and heat, although the significance of these quantities is still controversial [2-6, 11-13, 21,22], which gives rises to contradictory formulations, (*Abbot* 1976, *Allis and Herlin* 1952, *Arzélies* 1968, *De Broglie, Callen* 1969, *Callen* 1987, *Curzon* 1979, *Copeland* 1982, *Fuchs* 1987, *Haase* 1969, *Landau* 1967, *Pauli* 1973, *Prigogine* 1968, *Kestin* 1966, *Serrin* 1986, *Truesdell* 1980, *Yuen* 1970). The conceptual difficulties associated with the physical significance of the First Law have been recently approached in the area of classic (non relativistic) Thermodynamics [3-6].

The processes analysed in this work make it possible to understand the difficulty of attributing a general physical sense to dW and dQ, although such quantities are identified in the literature with the elementary quantities work and heat commonly taken as signifying "energy transfer".

1 THE DIFFICULTY OF ATTRIBUTING A PHYSICAL SIGNIFICANCE TO QUANTITIES WORK AND HEAT IN THE FIRST LAW OF THERMODYNAMICS FOR AN ISOTHERMAL QUASI-STATIC PROCESS.

Let us consider the following picture



One mole of an ideal gas expands from pressure p until the pressure becomes equal to the atmospheric pressure p_0 [1]. The initial and final temperature is T_0.

* Por lapso este artigo não saiu na Técnica "Número Único de 1993 – Abril de 1994" entendendo-se que dá continuidade à matéria tratada no referido número.

Assuming that the pressures are not too different, that the piston thermal conductivity is large enough and that there exists a frictional force between the piston and the cylinder wall, Abbot consider the process "quasi-static" and isothermal [1]. Of course if during the process the temperature is T_0 we have

$$dU = -pdV + T_0 dS \qquad (1)$$

In fact, if $U=U(S,V)$, $$\boldsymbol{d}U = \left(\frac{\partial U}{\partial V}\right)_S \boldsymbol{d}V + \left(\frac{\partial U}{\partial S}\right)_V \boldsymbol{d}S \qquad (2)$$

where $\boldsymbol{d}$ is the exterior derivative operator [26], $-(\partial U/\partial V)_s=+p$ is the pressure and $(\partial U/\partial S)_v=T=T_0$ is the temperature, constant and equal to the atmosphere temperature during the process.

We therefore have $$dU = \langle \boldsymbol{d}U, \boldsymbol{dP} \rangle \qquad (3)$$

where $\boldsymbol{dP}=dV\boldsymbol{I}+dS\boldsymbol{J}$ is an elementary displacement in space of variables V and S.

Relation (1) is valid, whether the expression of the first law $dU=dW+dQ$ has or not a physical significance [3-6].

It is however, usual to state the validity of

$$dW = -pdV \qquad (4)$$

and of $$dQ = TdS \qquad (5)$$

in a "quasi-static" transformation [1,14,15,23,28], although (4) and (5) are only valid in a reversible transformation ([18,3,4,5,6]).

Let us consider *by an absurd assumption(the assumption of Abbot and Van Ness)* that, in the transformation considered, $dU=dW+dQ$, where dW and dQ are given by (4) and (5).

The volume variation, after the piston is unblocked, is

$$\Delta V = V_2 - V_1 = \frac{RT_0}{p_0} - \frac{RT_0}{p} \qquad (6)$$

where V_2 and V_1 are the final and initial volumes of the gas.

Assuming (4) [1,25] , the atmosphere "work" is $W_0=p_0(\Delta V)$, we have

$$W_0 = \frac{RT_0}{p}(p - p_0) \qquad (7)$$

Considering that the internal energy is only a function of temperature, and $\Delta U+\Delta U_0=0$ between two equilibrium points, we have $\Delta U_0 = 0 = W_0 + Q_0$, Hence $Q_0 = -W_0$.

By making the entropy variation $\Delta S_0 = Q_0/T_0$ we have

$$\Delta S_0 = -\frac{R}{P}(p - p_0) \qquad (8)$$

If adopting the same procedure with gas [1], and assuming that the thermal conductivity of the walls is so high that T_0 is the temperature which can be considered to exist throughout the "quasi-static" process we shall have

$$dU = 0 = dW + dQ, \quad dQ = -dW, \quad dQ = pdV, \quad dQ = \frac{RT_0}{V}dV.$$

By making $dS = {}^{dQ}\!/\!_{T_0}$ we have

$$\Delta S = R \ln \frac{V_2}{V_1} = -R \ln \frac{p_0}{p} \tag{9}$$

In this way $$Q = T_0 \Delta S = -RT_0 \ln \frac{p_0}{p} \ .$$

is different [1] from $$-\mathrm{Q}_0 = -\mathrm{T}_0 \Delta \mathrm{S}_0 = -\frac{\mathrm{RT}_0}{\mathrm{p}}(\mathrm{p} - \mathrm{p}_0) \ .$$

If these quantities (Q and Q_0) have the physical significance of "heat exchange" between the two subsystems we have clearly a paradox. Without introducing a frictional force that may account for the slowness of the piston movement and for the inequality of ($-Q_0$) and Q [1], we think it is necessary to discard the identification of dW with $-pdV$ and of dQ with TdS, except in well defined conditions with an obvious physical significance [3-6]. However, for such situations, the energy conservation law is sufficient [4,5,6,11,12].

The entropy changes (8) and (9) can be calculated with relation (1). The relation (5) ($dQ=TdS$) is only a mathematical relation. It is also important to note that the "quasi-static" condition is not necessary for the validity of (8) and (9), because the entropy change is the same for whatever process between the same equilibrium points.

2 RESOLUTION OF AN ENTROPY MAXIMIZATION CONTROVERSY

Another related and subtle error in this matter can be found in the paper of *Curzon and Leff* published in *AJP*[18]. The authors claim to have resolved an entropy maximisation controversy. The model considered is a composite system consisting of two "adiabatically" isolated subsystems separated by a movable impermeable pistonlike wall (we obtain the "atmospheric" pressure p_0 from the previous example if one of these subsystems is large enough). If the piston is blocked there is no flux of energy between the subsystems although the temperature of subsystems 1 and 2 can be different.

Using the *Curzon and Leff* notation and meanings we can write for subsystems 1 and 2

$$S = S_1(U_1, V_1) + S_2(U - U_1, V - V_1) \ , \tag{1}$$

$$dS = dS_1 + dS_2 > 0 \tag{2}$$

and

$$T_1 dS_1 = dU_1 + p_1 dV_1 \ , \tag{3}$$

$$T_2 dS_2 = dU_2 + p_2 dV_2 \ . \tag{4}$$

But *Curzon and Leff* adopt the "first law", admitting obvious and a priori meanings for dQ_i and dW_i

$$dQ_i = dU_i + dW_i \ . \tag{5}$$

Although they realise that "(5) is not generally equivalent term by term to (3) and (4)" (these authors explicitly refer Callen's error), they commit another subtle error. Once again this error has its origin in the "first law" equation and in the connection between the "first" and the "second law" [3-6].

If we add (3) and (4), assuming the piston kinetic energy change is zero because we are considering two points where the piston is at equilibrium (see Appendix)

$$T_1 dS_1 + T_2 dS_2 = (p_1 - p_2) dV_1 \ . \tag{6}$$

If $p_1=p_2$, then $T_1dS_1+T_2dS_2=0$ and, of course, if $T_1 \neq T_2$, $dS>0$. We can have a process if $dS>0$ and this can be obtained with $dS_1.dS_2<0$. If $T_1>T_2$ we obtain $T_1dS_1+T_2dS_2=0$ with $dS_1<0$ and $dS_2>0$. If $T_1>T_2$ the piston, as Feynman pointed out [3-6,21,32], transfers energy from subsystem 1 to subsystem 2. This energy transfer with a zero thermal conductivity (if the piston is blocked no energy flows from 1 to 2) is obviously a gedanken experiment, but we can easily obtain (from the initial conditions $p_1=p_2=p$ and $T_1>T_2$) the equilibrium condition imposing $T_1=T_2=T$. This transformation has variations, $\Delta S>0$ and $\Delta S_1<0$ (the energy and the volume of subsystem 1 decrease).

Curzon and Leff reach another conclusion. They affirm that the existence of an irreversible process with $p_1=p_2$ is impossible. This is not so as stressed above.

The absurdity originates in equation(5) and (6) of *Curzon and Leff's* paper.

In fact, *Curzon and Leff* write (they refer *de Groot and Mazur*, *A. Katchalsky*, and *Glandsdorff* and *Prigogine*).

$$T_i dS_i > dQ_i \qquad (i=1,2)$$

Then, if we assume (as *Curzon and Leff* do) that dQ_i has a clear physical meaning, for an "adiabatic" piston $dQ_i=0$ and $T_idS_i>0$.

The entropy principle only imposes that

$$dS = dS_1 + dS_2 > 0$$

This can be achieved with $T_1dS_1<0$ and the conclusion of *Curzon and Leff* about the inequality of the pressures p_1 and p_2 is obviously false.

Since $$dS = dS_1 + dS_2 > 0$$

it is possible to achieve and reconcile *Feynman* result based on a microscopic kinetic analysis (the equality of pressures and temperatures, $p_1=p_2$ and $T_1=T_2$) with an energy-entropy formulation [9,3-6].

In fact only when the system attains equilibrium, $dS=0$ (it is interesting to see *Callen's* analysis based on the first law [15]). Therefore

$$dS = dS_1 + dS_2 = \frac{p_1}{T_1}dV_1 + \frac{dU_1}{T_1} + \frac{p_2}{T_2}dV_2 + \frac{dU_2}{T_2}$$

with $dV = dV_1 + dV_2 = 0$ and $dU = dU_1 + dU_2 = 0.$

This being so $$dS = dS_1 + dS_2 = \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)dV_1 + \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU_1$$

The equilibrium condition $dS=0$ leads to $T_1=T_2$ and $p_1=p_2$ [15]. *Feynman's* analysis is correct but *Callen's and Curzon's* is not (see Appendix 2).

CONCLUSIONS

Two processes have been used to show that the First Law introduced by *Clausius* [13,22] leads to separate the energetic interaction into work and heat terms [14,15,18,19].

The separation of the energetic interaction between two subsystems by dividing it into work and heat terms, cannot have a precise and general significance [34]. We have analysed two particular cases which can help to understand the difficulty of this separation.

A terminology corresponding to well-defined physical entities is of fundamental importance for the study of the interaction between subsystems [4-6]. We are firmly convinced that the First Law of Thermodynamics introduced by *Clausius*[22] gives rise to formalisms whose physical significance, as demonstrated through two particular cases, cannot be generalised (see Appendix 2).

Appendix 1

If the piston kinetic energy change is not zero ($dE_{kin}=0$) we have $dU_1+dU_2+dE_{kin}=0$.

But $dE_{kin}=+p'_1dV_1+p'_2dV_2$ where p'_1 and p'_2 , the pressures on the moving piston, are equal to p_1 and p_2 when the piston component velocity $\dot{x}_1$ is equal to zero.

Therefore when $\dot{x}_1 = 0$ we have

$$-p_1dV_1 + T_1dS_1 - p_2dV_2 + T_2dS_2 = -p'_1\,dV_1 - p'_2\,dV_2$$

or

$$T_1dS_1 + T_2dS_2 = 0\,.$$

If $\dot{x}_1 \neq 0$,

$$T_1dS_1 + T_2dS_2 = \left(p_1 - p_1^{'}\right)dV_1 + \left(p_2^{'} - p_2\right)dV_1\,.$$

If $p_1>p_2$ then $dV_1>0$, $p'_1<p_1$ and $p'_2>p_2$.

If $p_1<p_2$ then $dV_1<0$, $p'_1>p_1$ and $p'_2<p_2$.

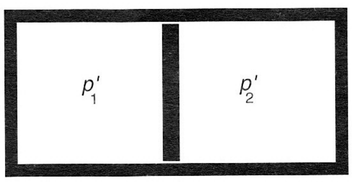
Therefore

$$T_1dS_1 + T_2dS_2 > 0\,.$$

Appendix 2

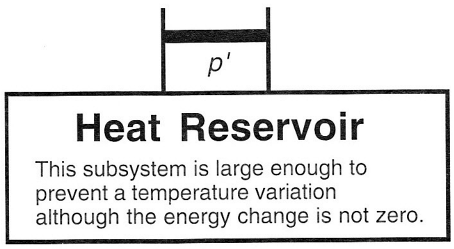
Why is this controversy not solved or, and this is even stranger, why do some authors refuse to accept the existence of difficulties although the existence of incompatible formulations is a fact? (see the comparison between some formulations in the second table below).

The following figure corresponds to the model considered in the text. Let's call this model, model 1.



Model 1

The other model we need to consider is represented on the following figure:



Model 2: the paradigm of thermodynamics... [4, 5]

For model 1, the pressures p'_1 and p'_2 are the dynamical pressures [5,8] at sides 1 and 2. We can write

$$dW_{diss} = d\overline{U} = dU_1 + dU_2\,.$$

If we choose as the "system" the subsystem 1, and if we make $U_1=U$, we have

$$\mathrm{dW}_{\mathrm{diss}} = \mathrm{dW}_{\mathrm{diss}_1} + \mathrm{dW}_{\mathrm{diss}_2} = \mathrm{dU} + \mathrm{dU}_2 \ .$$

Obviously, we can (as always!), write

$$-dW_{diss_1} + \underline{\underline{d}}Q_1 = dU_1 \qquad \text{and} \qquad -dW_{diss_2} + \underline{\underline{d}}Q_2 = dU_2$$

and, of course $\underline{\underline{d}}Q_1 + \underline{\underline{d}}Q_2 = 0, \quad dW_{diss_i} = -p'_i dV_i \qquad (i=1,2).$

But, we can also write

$$dU = -pdV + TdS \qquad \text{and} \qquad dU = \text{đ}W + \text{đ}Q$$

with

$$\text{đ}W = -pdV \qquad \text{and} \qquad \text{đ}Q = TdS \ .$$

Therefore, we can write

$$dU = -p'\,dV + \underline{\underline{d}}Q = \underline{\underline{d}}W + \underline{\underline{d}}Q \ ,$$
$$dU = -pdV + TdS = \text{đ}W + \text{đ}Q \ .$$

But, for model 2, and for a reversible transformation we have

$$dW = \text{đ}W = \underline{\underline{d}}W = -pdV,$$
$$dQ = \text{đ}Q = \underline{\underline{d}}Q = TdS$$

With generality, we have only

$$-p'\,dV + \underline{\underline{d}}Q = -pdV + TdS,$$
$$-(p' - p)dV = TdS - \underline{\underline{d}}Q.$$

If $dV<0$, $p'\geq p$

(= if the transformation is reversible).

If $dV>0$, $p'\leq p$, then

$$TdS - \underline{\underline{d}}Q \geq 0 \Leftrightarrow TdS \geq \underline{\underline{d}}Q$$

For model 2, we have

$$dQ = \underline{\underline{d}}Q \ \text{(in fact } d\overline{U} = dU + dU_F = -p'\,dV = dU - dQ \text{)} \qquad [5]$$

and, therefore $TdS \geq dQ$.

For a adiabatic (model 2) $dQ = 0$ and, therefore $dS \geq 0$.

with $\underline{\underline{d}}Q_i \geq 0$

For model 1, we have $T_i dS_i \geq \underline{\underline{đ}}Q_i$ or $\underline{\underline{d}}Q_i \leq 0$ (i=1,2) as long as $dS = dS_1 + dS_2 \geq 0$ is verified.

The several infinitesimal quantities have integrals between near points, approximately equal. This explains why the experimental results agree with an approximate theory. Of course we can have a cumulative effect and the integrals are completely differents IF THE POINTS ARE SUFFICIENTLY DISTANT [7,8] (about the meaning of physically small quantities and mathematics see the interesting article of *Francine Diener and Marc Diener*, Les applications de l'ánalyse non standard, *La Recherche,* 206, 1989).

The following table summarises some of the possible concepts of heat.

Table I *Possible concepts of heat*

Heat 1	Internal Energy U	$W=\Delta U$
Heat 2	Heat exchange	$dQ=-dUF$
Heat 3	Heat 3 $đQ$	$dU=-pdV+đQ$
Heat 4	Heat 4 $\underline{\underline{d}}Q$	$dU=-p'dV+\underline{\underline{d}}Q$
Heat 5	Heat 5 dQ_5	$dU=-p_{ext}dV+dQ_5$

The following table gives some typical examples of different formulations of thermodynamics (*Allis and Herlin* formulation is remarkable).

Table II *Different formulations of thermodynamics*

Author	*Allis*	*Huang*	*Reif*	*Callen Ed. 1987*	*Rumer & Rivkin*
Quasi-static	slow	Equilibrium points	Equilibrium points	Equilibrium points	Equilibrium points
Reversible	$dW=-pdV$ QS is not equivalent to reversible (p. 85) Q.S.≠>Rev. Rev.≠>Q.S.	The transformation can be reversed. Rev.=>Q.S. Q.S.=>Rev.	The transformation can be reversed versed. p. 93 Rev.⇏Q.S. Q.S.=>Rev.	The transformation can be reversed Q.S.≠>Rev. Rev.=>Q.S.	The transformation can be reversed. Q.S.=>Rev. Rev.=>Q.S.
Work	$dW=-pdV$ For a reversible	$dW=-pdV$ For a reversible see p. 4 and 7	$dW=-pdV$ For a reversible (or quasi-static)	$dW=-pdV$ For a reversible	$dW=-pdV$ For a reversible or irreversible transformation
Heat and the First Law	$dQ=dU-dW$ $dQ=TdS$ for rav. $dU=-pdV+T$ dS for rev.	$dQ=dU-dW$ $dQ=TdS$ for rev. $dU=-pdV+T$ dS for rev.	$dQ=dU-dW$ $dQ=TdS$ for rev. or Q.S. $dU=-pdV+T$ dS for rev. or Q.S.	$dQ=dU-dW$ $dQ=dU+pdV$ This expression is valid for Q.S. $dQ=TdS$ for Q.S.	$dQ=dU+pdV$ This expression is valid for QS or for irreversibles. $dQ=TdS$ only for a QS

Each author is partially correct. Because each one partially knows the inconsistency of other formulations they try to solve the points they know are incorrect. Of course a synthesis can be achieved.

For example, *Allis, Herlin* [10] and *Huang* [24] know the incorrectness of thinking of a quasi-static transformation as a reversible one (*Reif* formulation [29]) or the incorrectness associated with $dQ=TdS$ for quasi-static irreversible transformations (*Callen* formulation). But *Callen* knows that $dU=-pdV+TdS$ is valid for "quasi-static" irreversible transformations. Then he wrote *Callen* [16]:

> *"A monoatomic ideal gas is permitted to expand by a free expansion from* V *to* V+dV *(recall problem 3.4-8). Show that*
>
> $$dS=\left(\frac{NR}{V}\right)dV$$
>
> *In a series of such infinitesimal free expansions, leading from* V_i *to* V_f *show that*
>
> $$\Delta S = NR\ln\left(\frac{V_f}{V_i}\right)$$
>
> *Whether this atypical (and infamous) "continuous free expansion" process should be considered as quasi-static is a delicate point. On the positive side is the observation that the terminal states of the infinitesimal expansions can be spaced as closely as one wishes along the locus. On the negative side is the realisation that the system necessarily passes through nonequilibrium states during each expansion; the irreversibility of the micro expansions is essential and irreducible. The fact that* dS>0 *whereas* dQ=0 *is inconsistent with the presumptive applicability of the relation* dQ=TdS *to all quasi-static processes. We define (by somewhat circular logic!) the continuous free expansion process as being "essentially irreversible" and non quasi-static."*

Callen refers to the criticism of a "continuous free expansion" (see for example *Allis, Herlin and Huang*) with the peculiarity of *Callen's* analysis, a quasi-static is not necessarily reversible but $dQ=TdS$ for a quasi-static (note that *Reif's* formulation is another, because he defines a reversible transformation as quasi-static).

But at p.15 *Callen* had prevent any possible internal inconsistency, the major criterium for evaluate science: "*In practice the criterion for equilibrium is circular. Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory!* " (The exclamation mark is due to *Callen*, not mine!)

By definition *Callen* says that a specific quasi-static process ("a succession of equilibrium points") is "nonquasi-static"! When the important point is that for this process $dU=-pdV+TdS$ is verified although $dW\neq -pdV$ and $dQ\neq TdS$, although $\text{đ}W=-pdV$ and $\text{đ}Q=TdS$. The quantities $\text{đ}W$ and $\text{đ}Q$ has not the physical significance that *Callen* thinks that must have and the analysis of *Callen's* book [15] about model 2 is a clear example of that. To save this, Callen affirms that a specific quasi-static process is non-quasi-static!

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