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A Revision of Clausius Work on the Second Law. 4. On the Refutal of Clausius Proof

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Abstract: Clausius arguments advanced to prove that in a reversible cyclical process the combined value of all the transformations therein occurring must be equal to nothing, are here refuted.

Keywords: Clausius proof, refutal.

Introduction

"A process which can in no way be completely reversed is termed *irreversible,* all other processes *reversible"* [1], the full requirement for qualifying as one or the other being given by the possibility or impossibility..."to restore everywhere the exact initial state when the process has once taken place" [1]. Thus, if in a reversible process the universe can be restored to its initial state it is because the possibility exists of precisely undoing whatever changes the original process brought forward in the universe. Now, the fact that identical but inverse reversible transformations produce identical but opposite effects allow us to realize that the only way of precisely canceling the effects caused in the universe by a particular reversible transformation is that of coupling the said transformation with its inverse. Once the coupling is complete the universe will find itself in its original state. The same situation obviously applies regarding the effects brought upon in the universe by a group of reversible transformations [i], [j], [k] ... The cancellation of the effects here produced calls for the coupling of the said group with another constituted by their respective inverses. These situations can be represented by eqs. 1 and 2 as follows:

[i] + [- i] = 0 (1)

[i] + [j] + [k] + ... + {[-i] + [-j] + [-k] +.......} = 0 (2)

V[i] + V[- i] = 0 (3)

V[i] + V[j] + V[k] +..... + {V[-i] + V[-j] + V[-k] +.....} = 0 (4)

The equality to zero of eqs. 1 and 2 represents the fact that no net changes remain in the universe as a consequence of the referred couplings. Whatever changes were brought upon by the forward transformations, they were precisely canceled by the reverse transformations. Equations 3 and 4 are, on the other hand, the re-expression of eqs. 1 and 2 in terms of the values of the transformations there shown. Their equality to zero comes from the obvious fact that identical transformations convey identical values, or in other words that the value of the inverse of a particular transformation is equal in magnitude but of opposite sign to that of the original transformation. On this perspective, a net or combined value of zero appears as a corollary, i.e. as a natural consequence of the return of the universe to its original state. In the discussion that follows when speaking of a transformation it should be understood that reference is being made of a reversible transformation.

The fact that no other transformation but its inverse can precisely cancel the effects brought originally upon by it, combined with the fact that the universe can only return to its original state if the changes that were originally produced in it are canceled, leads to the realization that the condition expressed in eqs. 1 or 2 is thus both the necessary and sufficient condition for the return of the universe to its original state. The net or combined value of zero for such an occurrence, as before stated, appears as a natural consequence to the said return, and on this regard it can be said that a net or combined value of zero is a necessary, however not a sufficient condition for the return of the universe to its original state. This can be understood once it is realized that the possibility exists for two different transformations (or group of transformations) [m] and [n] to have the same value. Since the effects by they produced are different, as correspond to different transformations, the coupling of [m] with [-n] even if producing a net or combined value of zero, will not bring the universe back to its original state.

Now, that a net or combined value of zero is the natural consequence above referred can be understood by realizing that *whatever* the particular values V[i], V[j], V[k]... of the forward transformations might be, in coupling them with their inverses we will *always* end up with a sum of values that in being constituted by terms of the form {V[i] - V[i]}, {V[j] - V[j]}, {V[k] - V[k]}... will *always* be equal to zero. This situation can be re-expressed by saying that even if the return of the universe to its original state calls for the coupling of identical but inverse transformations, it however puts no restriction or condition on the individual values of the transformations involved nor calls for a particular relationship, beyond that given by eq. 4, between those values. Being this so it thus follows that from the return of the universe to its original condition no inference can at all be made regarding the particular values of the transformations involved nor about the existence of a particular relationship between those values, beyond that expressed by eq. 4. In short, the *only* inference (however worded) that from such an occurrence can be made regarding the values of the transformations involved is that the combined value of all of them is equal to zero. No other knowledge beyond this can be obtained from the sole fact of the return of the universe to its original state.

Clausius Basis of Proof

For Clausius the...”proof that in a reversible cyclical process the total value of all the transformations must be equal to nothing” [2], rests on the possibility of ...”the given transformations ...(being)...performed backwards” [3]. For him, if the transformations of a reversible cyclical process can be done backwards is proof that their sum is zero. In what follows, and keeping in mind the introductory discussion above given, a closer look will be taken at his proof.

Let us start by representing as [j] and [k] the two transformations associated to a simple reversible cyclical process, i.e.

$$[\ j\ ] = [Q(T)\rightarrow w] \quad \text{and} \quad [\ k\ ] = [Q^*(T)\rightarrow Q^*(T')] \qquad (5)$$

with T and T’ respectively standing for the temperatures of the hot and cold reservoir, and let us refer to the process constituted by these two transformations as the forward process. Accordingly, the transformations associated to the inverse of this process can be represented as follows:

$$[-j\ ] = [w\rightarrow Q(T)] \quad \text{and} \quad [-k\ ] = [Q^*(T')\rightarrow Q^*(T)] \qquad (6)$$

and we will refer to this as the reverse process.

Being this so, the concatenation of the forward and reverse processes takes the following form:

$$\{[\ j\ ] + [k\ ]\} + \{[-\ j\ ] + [\ -\ k\ ]\} = 0 \qquad (7)$$

and in it the equality to zero expresses the fact that the universe is returning to its original state as a consequence of the reverse process containing the inverse of each and every one of the transformations contained in the forward process.

It should now be realized that the re-expression of eq. 7 in terms of the values of the transformations will lead us to the mathematical representation of Clausius basis of proof, i.e. to the equation that expresses the return of the universe to its original state in terms of the combined values of the transformations of the forward (f), and reverse (r) processes, i.e.

$$\sum_f V_f + \sum_r V_r = 0 \qquad (8)$$

with $V_f = V_j + V_k$ and $V_r = V_{-j} + V_{-k}$ (9)

Let us now, in compliance with Clausius contention that the values of the transformations associated to a simple reversible cyclical process...”are equal in magnitude but of opposite sign...” [4], represent those values as follows:

$$V[\ j\ ] = a, \quad V[\ k\ ] = -a, \quad V[\ -j\ ] = -a, \quad V[-k\ ] = a \qquad (10)$$

and let us substitute those values on the mathematical representation of Clausius basis of proof, i.e. in eq. 8. When this is done, the following result is obtained:

$\{ a - a \} + \{ -a + a \} = 0$ (11)

from which it can be clearly seen that the said basis of proof is indeed satisfied by Clausius values, and this fact would indeed constitute solid proof for Clausius contention had those values been the *only ones* satisfying the said equation. This, however, does not happen to be the case, i.e. the same result will be obtained for *any* set of values one might want to assign to the said transformations. To see this let the values of the transformations be as follows:

$V[j] = x, \quad V[k] = y, \quad V[-j] = -x, \quad V[-k] = -y$ (12)

with x and y being any two values whatsoever. When those values are substituted in the equation of proof , we obtain, after rearrangement, the following result:

$\{ x + y \} - \{x + y \} = 0$ (13)

and from it an obvious conclusion follows: *any* set of values we might devise for the transformations will indeed satisfy the equation of proof. The situation represented in eq. 13, which was brought up in the introductory discussion, can also be understood by referring to a modified form of the equation of proof, i.e.

$\{V[j] - V[j]\} + \{V[k] - V[k]\} = 0$ (14)

And on reason thus of the fact by it expressed, i.e that the equation of proof is reducible to a sum of terms each of which represents the subtraction of a quantity from itself, it can then be concluded that the final result of such a sum, independently of the magnitudes of the said quantities, will always be equal to zero.

In terms of the matter under consideration these results indicate thus that Clausius basis of proof serves equally well for his values as for any other values whatsoever. In being thus incapable of discriminating between the real values of the transformations involved and any other set of values that to they might be ascribed, it thus follows that the said method of proof happens not to be so. Consequently, whatever proposition taken as true on such a basis, such as Clausius contention above quoted, should be disregarded as such.

The discussion just given has rendered Clausius basis of proof as non valid. Notwithstanding this, we will tackle and disprove his arguments one by one. This is the matter of the following sections.

The First Argument

According to Clausius [2]:

> If the cyclical process under consideration is reversible then, however complicated it may be, it can be proved that the transformations which occur in it must cancel each other, so that their algebraical sum is equal to nothing. For let us suppose that this is not the case, i.e. that their algebraical sum has some other value; then let us imagine the following process applied. Let all transformations which take place be divided in two parts, of which the first has its algebraical sum equal to nothing, and the second is made up of transformations all

having the same sign. Let the transformations of the first division be separated out into pairs, each composed of two transformations of equal magnitude but opposite signs.....The two transformations of each pair are now capable of being done backwards by one or two cyclical processes of the form described before.

Thus in the first place let the two given transformations be of different kinds, e.g. let the quantity of heat Q of temperature T be transformed into work, and the quantity of heat Q_1 be transferred from a body K_1 of temperature T_1 to a body K_2 of temperature T_2. The symbols Q and Q_1 are here supposed to represent the absolute values of the quantities. Let it also be assumed that the magnitudes of the two quantities stand in such a relation to each other that the following equation will hold, viz.

$$-\frac{Q}{T}+Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=0 \tag{15}$$

Then let us suppose the Cyclical Process to be performed in the reverse order, whereby the quantity of heat Q, of temperature T, is generated out of work, and another quantity of heat is transferred from the body K_2 to the body K_1. This latter quantity must then be exactly equal to the quantity Q_1, given in the above equation, and the given transformations have thus been performed backwards.

The Refutal

Let it first of all be acknowledged that the numbers 15, 16 and 18 do not appear in the corresponding equations in Clausius work. They were here assigned in order to maintain the logic flow of the discussions that follow.

Let us now re-enter into Clausius argument at the point in which the cyclical process is...”to be performed in the reverse order, whereby the quantity of heat Q of temperature T is generated out of work, and another quantity of heat is transferred from the body K_2 to the body K_1 ...” and let us designate this ‘another quantity of heat’ just referred, as Q*. Now, It is with regard to this quantity Q* that the following will be said: First, Q* can not be larger than Q_1 because it would imply a net transference of heat from a lower to a higher temperature, which is contrary to experience. Secondly, Q* can not be smaller than Q_1 because it would imply that a quantity of heat (Q_1 - Q*) beyond that required in a reversible operation has been transferred from the hot to the cold reservoir. This in turn would imply the forward cycle being irreversible when by definition we know it is reversible. If Q* is thus neither larger nor smaller than Q_1, it must then be equal to Q_1 and ...“the given transformations have thus been performed backwards”.

As seen, the reaching of such a conclusion requires of no assumption at all regarding the existence of a particular relationship between the values of the two transformations involved, such as that introduced by Clausius in the above argument through eq. 15.

The return of the universe to its original state was thus accomplished because the transformations of the reverse process precisely canceled the effects of those of the forward process, fact that, as has already been demonstrated, places no restriction on the particular values of the transformations nor calls for the existence of a particular relationship, beyond that given by eq. 4, between those values.

The Second Argument

Let us return to Clausius argument of proof [3]:

> ...Again let there be one transformation from work into heat and one from heat into work, e.g. let the quantity of heat Q of temperature T be generated out of work, and the quantity of heat Q' of temperature T' be transformed into work, and let these two stand in such a relation to each other that we may put
>
> $$\frac{Q}{T} - \frac{Q'}{T'} = 0 \quad (16)$$
>
> Then let us suppose in the first place that the same process as last described has been performed, whereby the quantity of heat Q of temperature T has been transformed into work, and another quantity Q_1 has been transferred from a body K_1 to another body K_2. Next let us suppose a second process performed in the reverse direction, in which the last-named quantity Q_1 is transferred back again from K_2 to K_1, and a quantity of heat of temperature T' is at the same time generated out of work. This transformation from work into heat must, independently of sign, be equivalent to the former transformation from heat into work, since they are both equivalent to one and the same transference of heat. The quantity of heat of temperature T', generated out of work, must therefore be exactly as great as the quantity Q' found in the above equation, and the given transformations have thus been made backwards.

The Refutal

Let us first of all recognize that eq. 16 is nothing more than the form Carnot's theorem adopts in the case at hand, and in such a form it establishes the condition to be fulfilled by the two heat-work transformations there referred when they are associated to the same (independently of sign) transference of heat. Through it Clausius manages to bring the universe back to its original state but in doing so, no new knowledge is brought forward that could support his claim regarding the values of the transformations of a simple reversible cyclical process being equal in magnitude but of opposite sign. In order to see this clearly let us translate into equations Clausius argument above given.

Let us then designate as [w→Q(T)] and [Q'(T')→w'] the first two transformations there introduced; as [Q(T)→w] and $[Q_1(K_1) \to Q_1(K_2)]$ those associated to the first cyclical process there referred and as $[Q_1(K_2) \to Q_1(K_1)]$ and as [w'→Q'(T')] the ones constituting the second cyclical process. On these terms the whole of Clausius argument can thus be represented as follows:

$$\{[Q_1(K_1) \to Q_1(K_2)] + [Q_1(K_2) \to Q_1(K_1)]\} + \{[w \to Q(T)] + [Q(T) \to w]\} + \{[Q'(T') \to w'] + [w' \to Q'(T')]\} = 0 \quad (17)$$

and from this expression one clear fact emerges; that the universe is returning to its original state because the effects of each one of the forward transformations have been precisely canceled by those of their respective inverses.

The fact that all the knowledge generated by the current Clausius argument is contained in eq. 17, combined with the already proven fact that from it no inference can at all be made regarding the values of the transformations allow us to render the said argument as futile and as such disregard it.

The Third Argument

Let us now re-enter into Clausius argument of proof [5]:

> .....Finally, let there be two transferences of heat, e.g. the quantity of heat Q_1 transferred from a body K_1 of temperature T_1 to a body K_2 of temperature T_2, and the quantity Q'_1, from a body K'_2 of temperature T'_2 to a body K'_1 of temperature T'_1, and let these be so related that we may put
>
> $$Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)+Q_1'\left(\frac{1}{T_1'}-\frac{1}{T_2'}\right)=0 \quad (18)$$
>
> Then let us suppose two Cyclical Processes performed, in one of which the quantity Q_1 is transferred from K_2 to K_1, and the quantity Q of temperature T thereby generated out of work, whilst in the second the same quantity Q is again transformed into work and thereby another quantity of heat transferred from K'_1 to K'_2. This second quantity must then be exactly to the given quantity Q'_1, and the two given transferences of heat have thus been done backwards.

The Refutal

Let us start by recognizing that eq. 18 follows directly from Carnot's theorem and in the case at hand it establishes the condition to be fulfilled by the two heat transferences there shown when they are associated to the same (independently of sign) heat-work transformation. Through it Clausius manages to bring the universe back to its original state but in doing so no new knowledge is brought forward that could support his claim regarding the values of the transformations. In order to support the statement just given we will proceed to translate into equations Clausius argument above transcribed.

Let us start by designating as $[Q_1(T_1) \to Q_1(T_2)]$ and $[Q'_1(T'_2) \to Q'_1(T'_1)]$ the first two transformations called into the argument; as $[Q_1(T_2) \to Q_1(T_1)]$ and $[w \to Q(T)]$ the two transformations associated to the first cyclical process there referred, and as $[Q(T) \to w]$ and $[Q'_1(T'_1) \to Q'_1(T'_2)]$ the two transformations associated to the second cyclical process. On these terms the whole of Clausius argument can thus be represented as follows:

$$\{[Q_1(T_1) \to Q_1(T_2)] + [Q_1(T_2) \to Q_1(T_1)]\} + \\ +\{[Q'_1(T'_2) \to Q'_1(T'_1)] + [Q'_1(T'_1) \to Q'_1(T'_2)]\} + \{[Q(T) \to w] + [w \to Q(T)\} = 0 \quad (19)$$

and from such an expression a clear fact emerges: that the return of the universe to its original state was accomplished because the effects of all the forward transformation were precisely canceled by their respective inverses.

The realization that the whole of Clausius knowledge advanced by the referred argument is contained in this equation, combined with the already proven fact that from such knowledge no inference can at all be made regarding the values of the transformations lead us to the same conclusion as before obtained for the second argument.

The Fourth and Last Argument

Let us quote Clausius last argument [6]:

> When by operations of this kind all the transformations of the first division have been done backwards, there then remain the transformations, all of the like sign , of the second division, and no others whatever. Now first, if these transformations are negative then they can only be transformations from heat into work and transferences from a lower to a higher temperature; and of these the transformations of the first kind may be replaced by transformations of the second kind. For if a quantity of heat Q of temperature T is transformed into work, then we have only to perform in reverse order the cyclical process above described, in which the quantity of heat Q of temperature T is generated out of work, and at the same time another quantity Q_1 is transferred from a body K_2 of temperature T_2 to another body K_1 of the higher temperature T_1. Thereby the given transformation from heat into work is done backwards, and replaced by the transference of heat from K_2 to K_1. By the application of this method we shall at last have nothing left except transferences of heat from a lower to a higher temperature which are not compensated in any way. As this contradicts our fundamental principle, the supposition that the transformations of the second division are negative must be incorrect.

> Secondly, if these transformations were positive, then since the cyclical process under consideration is reversible, the whole process might be performed in reverse order; in which case all the transformations which occur in it would take the opposite sign, and every transformation of the second division would become negative. We are thus brought back to the case already considered, which has been found to contradict our fundamental principle.
>
> As then the transformations of the second division can neither be positive nor negative they can not exist at all; and the first division, whose algebraical sum is zero, must embrace all the transformations which occur in the cyclical process.

Since, as Clausius himself has proved [7], a however complicated reversible cyclical process can always be reduced to a certain number of simple reversible cyclical processes to each of which two transformations are associated, it then follows that no reversible cyclical process, however complicated, is capable of producing unpaired transformations. Now, Clausius argument above quoted calling for the existence of a second division constituted by transformations all of the same sign requires in turn the existence of reversible cyclical processes capable of producing unpaired transformations. The fact that no such process is possible renders this last argument as trivial, and as such should be disregarded.

Conclusion

Clausius ..."proof that in a reversible cyclical process the total value of all the transformations must be equal to nothing" [2] rests on the possibility of those transformations being performed backwards. For him, if the transformations of a reversible cyclical process can be done backwards is proof that their sum is zero. Clausius proof is however here dismissed on the grounds that the possibility of the transformations being done backwards is independent of the individual values of the said transformations and consequently that from such an occurrence no inference can at all be made regarding those values.

By demonstrating that the analysis to it leading was a flawed one, the first three papers of this series have disproved Clausius contention claiming that in every simple reversible cyclical process the values of the transformations..."must be equal in magnitude but of opposite sign, so that their algebraical sum is zero" [4]. In this final paper the method of proof through which Clausius was trying to establish the veracity of the said contention, has also been disqualified. Through what we have called 'the negentropic formulation of the second law of thermodynamics' we have advanced, among other things, the true values of the transformations associated to a simple reversible cyclical process. If the paradigm supplied by this formulation is to be firmly established however, it will have to be through the expedient of translating the results by it provided into ....."propositions which may be proved or disproved by experiment" [8], because, after all, as Planck has also clearly stated... "Experiments are the only means of knowledge at our disposal. The rest is poetry, imagination." [9]. Some of the results of this task, including those related to Benard's convection efficiency, will be reported in the near future.

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