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**MECHANICAL FORMULATION
OF THE ENTROPY
OF A SYSTEM**

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1. INTRODUCTION.

What is entropy? We have been dealing with this concept since CLAUSIUS, but it is still obscure, probably because it is extraordinarily abstract, as Henri Poincaré affirmed. With BOLTZ-MANN's investigations, at the dawn of this century, something more of its significance was understood as a result of the statistical study of the problem. Entropy was defined according to the thermodynamic probability W :

$$S=kLnW+S_0$$

BOLTZMANN's constant is k ; with the advantage that S_0 is not indeterminate, as in the classical definition.

This study seeks to arrive at a mechanical understanding of the problem of entropy, based on the principle of energy conservation in an isolated system and on the concepts of *kinetic energy* and *potential energy* in which the internal energy of the same is definitively transformed.

We particularly noticed the necessity for internal energy to be additive in order for BOLTZMANN's principle to be applied, enabling us to find the canonical distribution of energy in a group of particles in statistical equilibrium. It must also be additive if we wish the entropy, in its classical definition, to be additive. That requirement is adopted in this study, together with the condition of the system being in equilibrium, in order to define the entropy.

On the other hand, the thermodynamic probability, W , of a macrostate, is closely connected to the corresponding "function of distribution of velocities", characterised by the parameter β , which in turn depends on

the average quadratic speed¹ v (r. m. s.), of the movement of molecules in the system. All this gave us reason to believe that there might exist a close relationship between the entropy, S , and the kinetic energy, U_c of the system.

The preceding considerations are of a basically heuristic nature, but this often occurs when problems are raised, many of which are subsequently solved by logical processes starting out from well established and defined principles.

In order to formulate the entropy of a system we must begin with the usual requirements:

- it must be *additive* or *extensive*.
- *increasingly monotonous* with the internal energy of the system.
- *without dimensions*.
- *homogeneous of first order*.

We shall also distinguish between a *simple system*, with all its parts being homogeneous among themselves, and a *composite system*, with two or more simple systems separated by barriers or walls, which may be either rigid or elastic. In this sense a system of this kind is heterogeneous. We shall define the entropy by starting with simple homogeneous systems in a procedure which is similar to the one used in statistical mechanics. It will generally suffice to consider composite systems made up of two *simple subsystems* since the results can immediately be extended to any number of them.

In the following sections we will expound the fundamental points, trying to avoid long-winded details for the sake of clarity and simplicity.

$$^1 \quad v = \sqrt{\frac{N_1 \mu_1 v_1^2 + N_2 \mu_2 v_2^2 + \dots + N_r \mu_r v_r^2}{N \mu}} \quad \text{con} \quad N \mu = \sum_i^r N_i \mu_i$$

2. INTERNAL ENERGY.

The *additivity* of the internal energy, U , of a system is frequently postulated, but it is a very demanding condition which the majority of real problems do not actually satisfy. Obviously this energy is the sum of two terms: kinetic energy, U_c , and potential energy, U_p , so that

$$U = U_c + U_p$$

The first is always additive and is defined by

$$U_c = \sum \frac{1}{2} m_i v_i^2 = \sum \frac{1}{2} N_i \mu_i v_i^2 = \frac{1}{2} m v^2$$

(with $m = \sum N_i \mu_i = \sum m_i$ and $v = \text{r.m.s. speed of the system}$)

When μ_i is the molar mass (or molecular if we are considering molecules) of each one of its parts or simple subsystems (in the case of a simple system, its homogeneousness requires that all the μ_i are equal). The second term, U_p , is generally made up of two parts: one additive and the other non-additive:

$$U_p = U_p^{addit} + U_p^{non\ addit}$$

Likewise, we can break up internal energy into two parts:

$$U = (U_c + U_p^{addit}) + U_p^{nonaddit}$$

The term in brackets corresponds to additive energy since U_c is always additive. Thus it can be seen that insisting that U must be additive is an excessive simplification; even in the ideal gases, whose internal energy is totally kinetic (principle of equipartition), since there is still the *potential of the elastic shock*, which, at least in part, is not additive since it depends on the number of shocks per unit of time and these depend on the average distance between molecules (according to the density, which varies with the volume v , in a closed system).

On the other hand, the fact that entropy is additive –in the classical formulation– means that internal energy must be so too. Since entropy is an *extensive* function it may only depend on the additive part of U , in the new formulation which is given below.

According to thermodynamics, internal energy can be expressed by the fundamental equation

$$U = U(S, v, N_1, \dots, N_r)$$

Function of the entropy, volume, and molar numbers. Since it depends on the volume v , it will not be additive in general, as volumetric variations entail the modification of distances of the different parts (or molecules) and, thereby, variation of the non-additive potential energy. If entropy, in accordance with the initial hypothesis, is a function –continuous, increasingly monotonous and which can be differentiated– of internal energy, we can write the preceding fundamental equation like this:

$$S = S(U, v, N_1, \dots, N_r)$$

and if the system is *isolated*, then the *internal energy*, U , is constant:

$$U = U_c + U_p = \text{constant}$$

as in the "First Principle". In this case the volume is also constant. It must also be

$$\left[\frac{\partial U}{\partial S} \right]_{v, N_1, \dots, N_r} > 0$$

when S is additive, it may only depend –directly– on the additive part of U and, as seen earlier, it will not depend on v either. We aim to find an expression for it which satisfies this condition. Thus it will be:

$$S = S(U^{addit}, N_1, \dots, N_r)$$

Indirectly it may depend on the non-additive energetic fraction, inasmuch as the kinetic energy U_c is in relation to this potential which influences its variations, and we have already seen that U_c is additive; but these are already included in its instantaneous value. The last expression can be written like this:

$$S = S(U_c + U_p^{addit}, N_1, \dots, N_r)$$

if we require that the system should be *closed*, it must then be

$$S = S(U_p + U_p^{addit}) \quad (\text{and "a fortiori" if it is } \textit{isolated})$$

As we shall see, entropy only makes sense in systems in steady equilibrium (or quasi-steady, that is, infinitely slow). Here we need an additional hypothesis, which is justified by the theorem of the virial in many cases, and the fact is that in each simple system it occurs that

$$U_p^{addit} = \textit{constant} \cdot U_c$$

The value of the constant coefficient will be *characteristic* of each system. Thus the preceding formulation gives this result:

$$U^{addit} = U_c + U_p^{addit} = U_c(1 + \text{constant}) = AU_c$$

and it is,

$$S = S(U^{addit}) = S(AU_c)$$

This conclusion is important, as it enables us to understand what entropy is, through a prism which is different from the customary ones based on caloric or statistical considerations.

In an isolated system, which is restrictive with regard to matter, energy and volume, it will be that $U = \text{constant}$, but the kinetic energy may vary and hence the entropy may also do so.

It will enable us to find the last functional dependence of S , with the condition of steady equilibrium, once we have defined the temperature of a simple and therefore homogeneous system.

3. TEMPERATURE OF A SIMPLE SYSTEM AND EXPRESSION OF ENTROPY.

We define temperature in the usual way, starting out from the condition of increasing monotony in relation to the internal energy:

$$T = \left[\frac{\partial U}{\partial S} \right]_{v, N_1, \dots, N_r} > 0$$

which in our approach to the problem and in an isolated system, can be written

$$T = \frac{\partial U^{addit}}{\partial S} = \frac{AdU_c}{dS} \quad [\text{with } U_c = \frac{1}{2}N\mu v^2]$$

Since we are dealing with a homogeneous system, all the molecules will be equal, with the same mass μ , so that the simple system's total mass will be

$$m = N\mu \quad (\text{when } N \text{ is the number of molecules})$$

We shall set the condition that the temperature has the dimensions of an energy which, in our case and given the simplicity of its expression, will be those of U_c ; it must moreover be an *intensive* function. The simplest expression is

$$T = a \frac{2U_c}{N} = a \frac{N\mu v^2}{N} = a\mu v^2$$

when, a , is a constant which is *characteristic* of each simple system and v the average quadratic speed (r. m. s.) of the molecules of which it is made up. From this expression and the preceding one we get the following result:

$$dS = \frac{AdU_c}{T} = \frac{Amvdv}{a\mu v^2} \frac{AN\mu dv}{a\mu v} = \frac{A}{a} N \frac{dv}{v}$$

whose immediate integration leads us to

$$S = \frac{A}{a} N L n v + S_0$$

equivalent to

$$S = \frac{AN}{2a} \text{Ln}(\frac{1}{2}mv^2) + \bar{S}_0 = \frac{AN}{2a} \text{Ln}U_c + \bar{S}_0 =$$

$$c \frac{N}{2} \text{Ln}U_c + \bar{S}_0$$

which is additive, can be differentiated and is increasingly monotonous with U_c , that is, with U^{addit} . It has no dimensions. The constant $c = A/a$ is likewise *characteristic* of each simple system.

It does not satisfy the NERNST-PLANCK axiom, since it takes infinite values when the temperature tends towards zero. In order to solve this difficulty the following expression can be put forward:

$$S^* = cN \text{Ln}(v+1) + S^*$$

whose first term is annulled with T , when $v \rightarrow 0$, but now the expression for the temperature will be somewhat different. In effect,

$$T^* = \frac{AdU_c}{dS^*} = \frac{AN\mu v dv}{cN \frac{dv}{v+1}} = a\mu v(v+1)$$

in which $T^* = T$ when $v \gg 1$. This last expression is valid in those real cases where the velocity satisfies this last condition, even when close to the absolute zero. It has the advantage that the level of reference S^* , does not remain undetermined; we can choose $S^* = 0$, when $T^* = 0$.

4. THERMIC EQUILIBRIUM IN A COMPOSITE SYSTEM.

For greater simplicity and still speaking in general terms, we shall imagine a composite system made up of two simple systems: (1) and (2). Its kinetic energy is

$$U_c = U_c^{(1)} + U_c^{(2)}$$

and the additive internal energy will be

$$U^{addit} = AU_c = A_1U_c^{(1)} + A_2U_c^{(2)} =$$

$$\frac{1}{2} A_1 N_1 \mu_1 v_1^2 + \frac{1}{2} A_2 N_2 \mu_2 v_2^2$$

the corresponding entropy will be

$$S = S^{(1)} + S^{(2)} = c_1 N_1 L n v_1 + c_2 N_2 L n v_2 + S_0$$

In order for there to be equilibrium, it is not enough that $dU = 0$, since the internal energy may be constant (total isolated system) and yet there may not be equilibrium. So another requirement is that the entropy should be extremal:

$$dS = dS^{(1)} + dS^{(2)} = 0$$

If the two simple subsystems we are looking at are separated from each other by rigid adiabatic walls, that also prevent matter passing through, they are then *independent*. Their internal energy is constant and if they are in steady equilibrium the entropy of each one will be so too. Let us suppose now that –without any transfer of matter– both systems start to interact, that is, they exchange energy (for instance, by means of a diathermic separation); the equilibrium ceases and the composite system evolves towards a new situation of equilibrium. If this is reached, it will be

$$dU = dU^{addit} + dU^{non\ addit} = 0$$

$$dS = dS^{(1)} + dS^{(2)} = 0$$

since the equilibrium is steady, then it is

$$dU^{addit} = 0 \quad dU^{non\ addit} = 0$$

which, together with the preceding condition, leads us to

$$dU^{addit} = dAU_c = A_1 N_1 \mu_1 v_1 dv_1 + A_2 N_2 \mu_2 v_2 dv_2 = 0$$

$$dS = c_1 N_1 \frac{dv_1}{v_1} + c_2 N_2 \frac{dv_2}{v_2} = \frac{A_1}{a_1} N_1 \frac{dv_1}{v_1} + \frac{A_2}{a_2} N_2 \frac{dv_2}{v_2} = 0$$

whose compatibility requires:

$$\left| \begin{array}{cc} \frac{\mu_1 v_1}{I} & \frac{\mu_2 v_2}{I} \\ \frac{1}{a_1 v_1} & \frac{1}{a_2 v_2} \end{array} \right| = 0$$

and from this

$$\frac{\mu_1 v_1}{a_2 v_2} = \frac{\mu_2 v_2}{a_1 v_1} \quad a_1 \mu_1 v_1^2 = a_2 \mu_2 v_2^2$$

that is to say, the temperatures of both simple systems must be equal as a necessary condition for equilibrium. This result can be extended to any composite system with a finite number of simple systems which interact with each other in the above-mentioned conditions.

5. ADDITIVE CHARACTER OF ENTROPY.

We looked first of all at a simple and thereby homogeneous system: all the molecules were equal with mass μ . In the preceding exposition we have tacitly assumed that the velocity was the same for all the N molecules of which it is made up. The entropy of each molecule is

$$s = cLn v + s_0$$

and for the whole system,

$$S = Ns = cNLn v + S_0$$

obviously in this case v coincides with the average quadratic speed of the system. But the fact of the matter is that, even with steady equilibrium, the speeds of the molecules are different, they are distributed (as in, for example, MAXWELL's distribution). In this case, to calculate the entropy we must proceed in the following way:

$$S = c_1Ln v_1 + \dots + c_NLn v_N + S'_0 = cLn(v_1v_2 \dots v_N) + S'_0$$

(taking the average value c). If we introduce the "geometric mean" of the speeds \tilde{v} , the result will be:

$$S = cLn \tilde{v}^N + S'_0 \quad \text{in which} \quad \tilde{v} = (v_1 v_2 \dots v_N)^{1/N}$$

And since S is determined at less than a constant S'_0 , it is also equivalent to

$$S = cLn(\mu\tilde{v})^N + \tilde{S}_0$$

Nonetheless, as we know, the "geometric mean" is less or equal to the "arithmetical mean" which in turn, because of CAUCHY-SCHWARZ's inequality, is less or equal to the "quadratic mean", so that

$$S = cLn(\mu\tilde{v})^N + \tilde{S}_0 \leq cLn \mu \left[\frac{v_1 + v_2 + \dots + v_N}{N} \right]^N + \tilde{S}_0 =$$

$$cLn(m\bar{v})^N + \tilde{S}_0 \leq cLn \left\{ \mu \left[\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N} \right]^{\frac{1}{2}} \right\}^N + \tilde{S}_0 =$$

$$cLn(mv)^N + \tilde{S}_0 = cN Ln v + S_{0\max} = S_{\max}$$

This maximum entropy, S_{\max} , cannot generally be obtained, since it is only possible when all the velocities are equal and thus it is evidently

$$\tilde{v} = \bar{v} = v$$

We have made this slight digression to demonstrate that entropy is additive with regard to the parts which we may consider in the system, if we express it according to the average geometrical velocity, \tilde{v} . It also serves to point out the existence of an upper limit, S_{\max} , (for the same kinetic energy U_c). However, it is perfectly possible to make S depend on the average quadratic velocity v , since the relationship between the three: \tilde{v} , \bar{v} , v , is in accordance with a constant coefficient which only affects the value of the reference S_0 (system in steady equilibrium).

We shall now look at what happens in a composite system made up of several simple subsystems. Let us suppose that we are dealing with n ; we shall have,

$$S = S^{(1)} + S^{(2)} + \dots + S^{(n)} =$$

$$c_1 N_1 L n v_1 + c_2 N_2 L n v_2 + \dots + c_n N_n L n v_n + S_0$$

in which v_1 and $v_2 \dots v_n$ are the corresponding average quadratic speeds (r. m. s.). As before, it is

$$S = c L n \left[\frac{v_1^{N_1} \cdot v_2^{N_2} \cdot \dots \cdot v_n^{N_n}}{N} \right] + S_0 = c L n \tilde{v} + S_0$$

(in which $N = N_1 + N_2 + \dots + N_n$). It is also shown here that:

$$S = c L n \tilde{v} + S_0 = c L n \left[(\mu_1 v_1)^{N_1} (\mu_2 v_2)^{N_2} \dots (\mu_n v_n)^{N_n} \right] + \tilde{S}_0 \leq$$

$$c L n \left[\frac{N_1 \mu_1 v_1 + \dots + N_n \mu_n v_n}{N} \right]^N + S'_0 = c L n (\mu \bar{v})^N + \tilde{S}_0 \leq$$

$$c L n \left\{ \mu \left[\frac{N_1 \mu_1 v_1^2 + \dots + N_n \mu_n v_n^2}{N \mu} \right]^{1/2} \right\}^N + \tilde{S}_0 = c L n (\mu v)^N + \tilde{S}_0 =$$

$$c N L n v + S_{o \max} = S_{\max}$$

(with $N_1\mu_1 + N_2\mu_2 + \dots + N_n\mu_n = \text{total mass} = N\mu$). The maximum entropy, S_{max} , can only be obtained if all the r. m. s. are identical in each subsystem, but this is not usually possible. However, as we saw earlier when dealing with the *two systems*, entropy reaches an extremal value when the system evolves from an *initial state* of equilibrium towards another *final state* of equilibrium, in which all the temperatures (at least in part) become equal, since $dS = 0$. Further on we shall see that if this second situation of steady equilibrium is obtained in an *isolated* system, the final entropy is greater than the initial entropy.

6. INCREASE OF ENTROPY IN AN ISOLATED SYSTEM.

The property of entropy being increasingly monotonous with the internal energy, U , of the system is expressed by:

$$T = \left[\frac{\partial U}{\partial S} \right]_{v, N_1 \dots N_r} = \frac{\partial U^{addit}}{\partial S} = \frac{AdU_c}{dS} > 0$$

(with $U^{addit} = U_c + U_p^{addit} = AU_c$, as we know, by hypothesis). Clearly, in these conditions, S increases and decreases according to whether U_c does so (at most, in an exceptional case it will remain constant). If the system remains energetically isolated, it will conserve its inner energy

$$U = U_c + U_p = \text{constant}$$

If U_p decreases, U_c will increase. If the system changes from one state of steady equilibrium to another one, also steady, the entropy must *increase*, since in Mechanics (Statics) steady equilibriums are those in which all the possible *virtual* movements of the system imply a *negative* work; for this reason, if the system evolves (having lost its steadiness) towards another

steady state, it means that U_p *decreases*; otherwise, this evolutionary process would not take place. The final entropy will be greater than the initial one, since it varies monotonously with U_c ; exceptionally it might remain constant as mentioned earlier. The impossibility of passing from one state of equilibrium directly to another one (both of them steady) without an increase in the entropy is the basis of the *irreversibility* of the process.

In this sense, thermodynamics is governed by the same laws of steady equilibrium as Mechanics (Statics). If the process is quasi-static it means that it is *reversible* at all times, thus $dS = 0$ and the entropy will therefore remain constant ($d^2S = 0$).

Obviously, the system can evolve without obtaining steady equilibrium, then the entropy will increase or decrease, passing through situations of unsteady equilibrium, of relative maximums or minimums (or points of inflexion of zero derivative), in which $dS = 0$, but the entropy does not obtain a constant value; it does not become stabilized and the system is *oscillating*. If there is *inner dissipation* the oscillation will diminish until a steady equilibrium is obtained.

We shall now analyse some specific paradigmatic cases that are useful to complete the preceding exposition.

We have already seen what corresponds to a *composite system* formed of two *simple subsystems*, separated by a rigid diathermic wall; the whole is isolated and rigid (see section 4.-). The temperature should be equal, it only had to be seen that the final entropy was greater than at the beginning. This is immediate, so we have:

$$U = AU_c + U_p^{non\ addit} = constant$$

but, since the volume remains constant in both subsystems, we get

$$U_p^{non\ addit} = constant$$

consequently

$$AU_c = A_1U_c^{(1)} + A_2U_c^{(2)} = U_c + U_p^{addit} = constant$$

if the system evolves it means that U_p^{addit} decreases and then S will increase.

7. ANALYSIS OF SOME COMPOSITE SYSTEMS.

a. Equilibrium in a rigid system made up of two simple systems, separated by a diathermic mobile wall (piston).

There is no flow of matter: the molar numbers are constant. The internal energy is also constant because we are considering it as an isolated whole. We have:

$$U = U_c + U_p^{addit} + U_p^{non\ addit} = constant$$

with

$$U_c = U_c^{(1)} + U_c^{(2)} \quad U_p^{addit} = U_p^{addit(1)} + U_p^{addit(2)}$$

$U_p^{non\ addit}$ cannot be broken down into different quantities since it is the group potential energy. The volumes may vary and satisfy

$$v^{(1)} + v^{(2)} = constant$$

Since entropy is additive, it only depends on the additive internal energy,

$$U^{addit} = A_1U_c^{(1)} + A_2U_c^{(2)}$$

and in steady equilibrium it must be,

$$dS = dS^{(1)} + dS^{(2)} = \frac{A_1 dU_c^{(1)}}{T^{(1)}} + \frac{A_2 dU_c^{(2)}}{T^{(2)}} = 0$$

together with:

$$dU^{addit} = A_1 dU_c^{(1)} + A_2 dU_c^{(2)} = 0 \quad (\text{and likewise, } dU_p^{non\ addit} = 0)$$

with the immediate result:

$$\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} = 0$$

The temperatures must be equal when steady equilibrium is obtained.

On the other hand, the non-additive potential satisfies

$$AU_c + U_p^{non\ addit} = \text{constant}$$

and the virtual work in the position of equilibrium must be zero:

$$p^{(1)} dv^{(1)} + p^{(2)} dv^{(2)} = 0$$

since it depends on the variation of the non-additive potential and this, as seen earlier, complies with

$$dU_p^{non\ addit} = 0$$

and being $d\mathbf{v}^{(1)} = -d\mathbf{v}^{(2)}$, it will be

$$p^{(1)} = p^{(2)}$$

Finally, the conservation of energy mentioned earlier on requires that, in steady equilibrium, $U_p^{non\ addit}$ should be minimum and the term AU_c should be maximum; the immediate consequence is that entropy grows when it passes from one state of steady equilibrium to another one which is also steady. This transition is possible because some constrictions disappear: the separating wall, formerly rigid and adiabatic, is replaced by another one which is mobile and diathermic.

b. A rigid isolated system made up of two subsystems separated by a rigid and perforated wall.

In this case the final equilibrium requires

$$dS = \frac{dU^{addit\ (1)}}{T^{(1)}} + \frac{dU^{addit\ (2)}}{T^{(2)}} = 0$$

and when in equilibrium:

$$dU^{addit} = dU^{addit\ (1)} + dU^{addit\ (2)} = 0$$

immediately,

$$T^{(1)} = T^{(2)}$$

Moreover, it is clear that in the final state it will be

$$p^{(1)} = p^{(2)}$$

On the other hand, both systems interact in such a way that the potential energy, $U^{non\ addit}$, which depends on the reciprocal positions of all its molecules, is minimum; otherwise, these would not be modified, and even less so in the exceptional case of all the initial positions being equivalent. Obviously, in this case the system is conservative, and U^{addit} is maximum in the new equilibrium. Thus it can be shown that

$$U^{addit} = U_c + U_p^{addit} = \text{maximum and constant}$$

The kinetic energy now depends only on U_p^{addit} which, by the same criterion, must be minimum. Thus, U_c increases and the entropy *grows*. We have tacitly assumed that, once the two subsystems are mixed, the starting hypothesis continues to be verified:

$$U_p^{addit(1)} = A_1 U_c^{(1)} \quad \text{and} \quad U_p^{addit(2)} = A_2 U_c^{(2)}$$

c. An isolated rigid system made up of two simple subsystems separated by a mobile adiabatic wall.

In this problem the conservation of internal energy is also shown:

$$U = U^{addit} + U^{non\ addit} = (U_c + U_p^{addit}) + U_p^{non\ addit} = \text{constant}$$

Here also the entropy depends on, U^{addit} , satisfying

$$U^{addit} = U^{addit(1)} + U^{addit(2)}$$

and furthermore,

$$T^{(1)} = \frac{dU^{addit(1)}}{dS^{(1)}} \quad T^{(2)} = \frac{dU^{addit(2)}}{dS^{(2)}}$$

However, in the present case, it cannot be affirmed that, in all virtual evolutions, $dS = 0$, $d^2S < 0$, is satisfied, even if it is true that

$$dU^{addit (1)} + dU^{addit (2)} = 0$$

in the possible steady equilibriums. As a result, the temperatures which correspond to the new state of equilibrium remain indeterminate; (if this state is obtained, since, if there is no internal dissipation of the exchanged work, the system will be oscillating).

On the other hand, the variations in volume comply with:

$$dv_1 = -dv_2$$

since the volume of the compound system is constant. As $U^{non addit}$ depends on the variations in volume, we can write

$$dU^{non addit} = dU_p^{non addit} = -p^{(1)}dv_1 - p^{(2)}dv_2$$

and in the state of equilibrium (if one is reached) the value of this potential must be *extremum*, so that:

$$p^{(1)}dv_1 + p^{(2)}dv_2 = 0$$

and when the volume is constant, we immediately get the result:

$$p^{(1)} = p^{(2)}$$

Thus we definitively prove the physical intuition that this question is only partially determined.

8. IDEAL GAS.

According to classical thermodynamics, in an isolated system it is:

$$U = U_c + U_p = \text{constant}$$

but now U_c and U_p are also constant.

There is no interaction amongst the molecules, so that $U_p^{\text{non addit}} = \text{constant}$; the potential of elastic shock is not taken into account and the internal potentials of each molecule, such as $U_p^{\text{addit vib}}$, etc, are considered as being included in U_c , on account of the energetic "principle of equipartition". From the thermodynamic paradigm that we are expounding, the entropy should be constant, whilst in the customary formulation it is:

$$S = kN \left[L \ln v + \frac{1}{2} L \ln T \right] + S'_0$$

(with $l = \text{degrees of freedom of the system}$).

And being $T = \text{constant}$, we shall get

$$S = knL \ln v + S''_0$$

that is to say, it only depends on the volume u . Nevertheless, in an ideal gas, seen in a way which is more in keeping with reality, there are: on one hand the elastic potential, which depends on the average distance between the molecules and also on their internal additive potentials (such as vibration), and

on the other hand the aforementioned inner potentials, which are additive. The elastic potential is then *non-additive* (at least in part). We may definitively write also for an ideal gas:

$$U_c + U_p^{addit} + U_p^{non\ addit} = constant$$

which in the new paradigm is reduced to:

$$AU_c + U_p^{non\ addit} = constant$$

The kinetic energy U_c of an ideal gas will not be constant now; when it expands it will *increase*—as will the entropy— so $U_p^{non\ addit}$ *decreases*. In the classical explanation this increase is caused by the increase in volume. When U_c varies, so will the temperature T , which increases with the expansion of the ideal gas, while it remains constant in the customary paradigm. The average quadratic speed v^* is constant in this case, and therefore different from the speed v , which defines U_c in the first.

Since both entropies must coincide, as we are dealing the same ideal gas seen from the point of view of different theories, we can write:

$$S = kN \ln v + S_0'' = cN \ln v + S_0$$

that is

$$v^k = constant\ v^c$$

If the system is *open*, quasi-static in its evolution, both of these thermodynamic paradigms are still applicable and then it is

$$S = kN(\ln v + \frac{1}{2} \ln T) + S_0' \equiv cN \ln v + S_0$$

which immediately gives us,

$$v^k T^{\frac{1}{2}} = \text{constant } v^c$$

From the statistical point of view analogous equivalences can be made:

$$S = k \ln W = cN \ln v + S_0$$

and it is

$$W^k = \text{constant } v^{cN}$$

This equality could be written whenever the internal energy is additive (closed system), since this is a condition for the application of "BOLTZMANN's principle". In this sense statistical thermodynamics is more restrictive.

9 THE NERNST-PLANCK PRINCIPLE.

As shown earlier on, one way of making entropy satisfy the NERNST-PLANCK principle is to define it in this way:

$$S^* = cN \ln (v+1) + S^*_0$$

and now we have

$$T^* = a\mu v(v+1) \quad (\text{instead of } T = a\mu v^2)$$

since both are annulled for $v = 0$. By way of an example, let's see what happens with hydrogen:

$$\mu_H = 1.67 \cdot 10^{-27} \text{ kg}$$

$$k = 1.4 \cdot 10^{-23} \text{ J/}^\circ\text{K}$$

In order to calculate v_H we can use the expression

$$v_H = \sqrt{\frac{3kT}{\mu}} = 10^2 \cdot 1.59\sqrt{T}$$

for 1°K we get $v = 159 \text{ m/s}$; even with 0.001°K , it is $v_H = 5 \text{ m/s}$
The differences between T and T^* are minimal:

$$\frac{T^*}{T} = \frac{v+1}{v}$$

which in the first case gives us

$$\frac{T^*}{T} = \frac{160}{159} = 1.006$$

and in the second,

$$\frac{T^*}{T} = \frac{6}{5} = 1.2$$

So far, the hypothesis seems acceptable.

10. CARNOT's CYCLE.

Here we are dealing with a compound system made up of four subsystems: a) the thermostat (1) at temperature T_1 , b) the thermostat (2) at temperature $T_2 < T_1$, c) the substance or *simple system* which follows the cycle, d) the system which absorbs mechanical work w . As a whole we shall consider it as being isolated. The mass of the *system* which follows the cycle is:

$$m = N\mu$$

When N is the number of *mols* (or *molecules* in this case) and μ is the molar (or molecular) mass. The cycle, closed by two *adiabatics* and two *isothermals*, can be considered as being broken down into infinitesimal cycles in their isothermal phases.

In each one of these the system absorbs internal energy at the high temperature of T_1 , and loses internal energy at the temperature $T_2 < T_1$, in contact with the corresponding thermostats (differential isothermal phases); the difference is changed into mechanical work dw . This internal energy is *additive*, so the thermostats transmit or absorb it whilst the *volume* remains constant and, as a result, the *non-additive* internal energy does not vary. Moreover, in the system which travels round the cycle, its volume does not vary in a closed cycle and its non-additive energy remains unchanged.

The total work w is, obviously, the sum or integral of these infinitesimal works dw .

For the conservation of energy, we have

$$dU^{addit(1)} + dU^{addit(2)} + dw = 0$$

the first two terms correspond to the energy of the thermostats (1) and (2), which the system absorbs or loses, respectively, with the temperatures T_1 and T_2 . In the phase of isothermal expansion, the system undergoes a differential increase in temperature –which is matched by an increase in the average

quadratic speed in its molecules, dv_1 , at the speed v_1 – and in the phase of isothermal compression, the variation is in the opposite direction –with an increase of dv_2 at speed v_2 – so that when the cycle is completed there is a return to the same temperature as at the start.

We can express the earlier variations in internal energy in accordance with the average quadratic speeds of the system v_1 , v_2 , corresponding to the temperatures T_1 and T_2 in which they occur. We shall have:

$$U^{addit} = AU_c$$

so that the first equation can be written

$$AdU_c^{(1)} + AdU_c^{(2)} + dw = 0$$

with

$$U_c^{(1)} = \frac{1}{2}N\mu v_1^2 \quad U_c^{(2)} = \frac{1}{2}N\mu v_2^2$$

The *efficiency* of CARNOT's cycle will be:

$$\eta = \frac{AdU_c^{(1)} + AdU_c^{(2)}}{AdU_c^{(1)}} = 1 + \frac{N\mu v_2 dv_2}{N\mu v_1 dv_1} = 1 + \frac{v_2 dv_2}{v_1 dv_1}$$

Since the evolution is quasi-static, the composite system and its subsystems are permanently in steady equilibrium: the entropy is constant in the isothermal phases and remains unchanged in each complete infinitesimal cycle. Let us take a more detailed look at this extreme: in the two adiabatic phases the total variation is zero, since the system returns to the initial speed (temperature) and the thermostats do not intervene. In each differential isothermal phase, there is a variation of the entropy in the system which follows the cycle –variations dv_1 and dv_2 of the average quadratic speed, (see fig.1)– but, as this remains constantly in thermic equilibrium (except for

infinitesimals) with the thermostats, the latter undergo equal and opposite variations of entropy; the entropy does not vary and, since the system returns to its initial condition, we can write

$$dS^{(1)} + dS^{(2)} = cNdv_1/dv_1 + cNdv_2/v_2 = 0$$

(the entropy of the simple system is $S = cNLnv + S_0$) and this gives the result

$$\frac{dv_1}{dv_2} = -\frac{v_1}{v_2}$$

and the *efficiency* can be expressed:

$$\eta = 1 - \frac{v_2^2}{v_1^2} = 1 - \frac{T_1}{T_2} \leq 1$$

($T = a\mu v^2$, as pointed out earlier).

Finally, it must be emphasized that the mechanical system, which absorbs work w (or supplies it if the cycle is functioning in the opposite direction), does not contribute to any variation in the entropy, as the velocities of the masses which make it up (piston, connecting rods, etc) are infinitely slow.

Only CARNOT's cycle, between two thermostats, can have the *efficiency* η which was found, since the equilibrium of the system with these thermostats requires that these two stages must be necessarily *isothermal*; in any other exchange of energy which is not isothermal the velocities v'_1 , will be less than or equal to v_1 , and the v'_2 will be greater than or equal to v_2 , so that,

average value of: $\frac{v_2'^2}{v_1'^2} > \frac{v_2^2}{v_1^2}$

and the *efficiency* will be less:

$$\eta' < \eta$$

The other two phases of the cycle must, likewise, be *adiabatic*, because the system is thermically isolated.

If the evolution of the system were not infinitely slow (quasi-static), no constant equilibrium would be able to exist between the system and the thermostats, nor within it in the adiabatic phases; nor would there be equilibrium with the system w , where mechanical work is released or absorbed: if its speed (or that of its component masses) were not infinitely slow, we should have to take into account its contribution to the variations of entropy (according to the new paradigm expounded here, which can be applied to any system of masses in movement). Therefore, in the adiabatic phases the evolution must also be quasi-static.

Being the equilibrium always constant, it is perfectly possible to invert the direction of CARNOT's cycle, it is *reversible*. In this case, we should have a "heat pump".

11. STABILITY.

For a *compound system* to remain in *steady* equilibrium it must be *isolated*. It must satisfy:

$$(U_p^{addit} + U_c) + U_p^{non\ addit} = U_0 = \text{constant}$$

Which with the initial hypothesis can be written

$$AU_c + U_p^{non\ addit} = U_0$$

The static equilibrium of the system requires that: $U_p^{non\ addit}$ reaches a *constant minimum* value in this state and, therefore, AU_c must be *maximum* and *constant*.

$$AdU_c = 0$$

But this condition is *not sufficient* for the system to be steady; the entropy can vary: increase, decrease or remain invariable. If the entropy is variable, obviously the system does not remain in equilibrium; the condition is *necessary*:

$$dS = 0$$

This *requirement* is not absolutely general; as we shall see, there may exist some system in steady equilibrium which does not comply with it (cases of *indetermination*).

Furthermore, we shall now see that it is *sufficient*. In every *virtual evolution* of the system in steady equilibrium the potential energy must undergo *positive* increases and U_c must decrease and also entropy, which must be *maximum* in steady equilibrium, that is:

$$d^2S < 0$$

To demonstrate this extreme we shall start with an isolated *composite system* made up of two *simple subsystems*, for the sake of simplicity and still speaking in general terms, as the result can be extended to any number of subsystems. We can show:

$$AU_c = \frac{1}{2}A_1N_1\mu_1 v_1^2 + \frac{1}{2}A_2N_2\mu_2 v_2^2 = \text{constant}$$

therefore,

$$AdU_c = A_1N_1\mu_1 v_1 dv_1 + A_2N_2\mu_2 v_2 dv_2 = 0$$

(extremum)

The second condition requires:

$$dS = d\left[\frac{A_1}{a_1}N_1 \ln v_1 + \frac{A_2}{a_2}N_2 \ln v_2\right] = 0 \quad (\text{extremum})$$

that is to say,

$$dS = \frac{A_1}{a_1}N_1 \frac{dv_1}{v_1} + \frac{A_2}{a_2}N_2 \frac{dv_2}{v_2} = 0$$

which with the preceding one leads us immediately to

$$a_1\mu_1 v_1^2 = a_2\mu_2 v_2^2$$

which, as we said earlier, expresses the condition of steady equilibrium

$$T_1 = T_2$$

It only remains to conclude that in all virtual evolutions $d^2S < 0$. We therefore differentiate, for the second time, the first and second condition. As U_c is constant, we shall have,

$$A_1N_1\mu_1(dv_1)^2 + A_2N_2\mu_2(dv_2)^2 = -(A_1N_1\mu_1 v_1 d^2v_1 + A_2N_2\mu_2 v_2 d^2v_2)$$

together with

$$d^2S = \left[\frac{A_1}{a_1} N_1 \frac{d^2 v_1}{v_1} + \frac{A_2}{a_2} N_2 \frac{d^2 v_2}{v_2} \right] - \left[\frac{A_1}{a_1} N_1 \frac{(dv_1)^2}{v_1^2} + \frac{A_2}{a_2} N_2 \frac{(dv_2)^2}{v_2^2} \right]$$

in which the second parenthesis is obviously > 0 . The first, by virtue of the preceding result and with $T_1 = T_2$, we can write

$$\begin{aligned} & \frac{A_1 N_1 \mu_1 v_1 d^2 v_1}{a_1 \mu_1 v_1^2} + \frac{A_2 N_2 \mu_2 d^2 v_2}{a_2 \mu_2 v_2^2} = \\ & \frac{1}{a_1 \mu_1 v_1^2} [A_1 N_1 \mu_1 v_1 d^2 v_1 + A_2 N_2 \mu_2 v_2 d^2 v_2] = \\ & \frac{-1}{T_1} [A_1 N_1 \mu_1 (dv_1)^2 + A_2 N_2 \mu_2 (dv_2)^2] < 0 \end{aligned}$$

so that the definitive result is:

$$d^2S < 0$$

thus we are dealing with a maximum of entropy which is obtained when the temperatures of both subsystems become equal.

If the constrictions do not vary the system will remain steady, but if they alter the system will evolve, its *entropy will increase*, until it reaches another state of relative maximum in which it will return to a state of

steadiness. If the initial temperatures of the subsystems remain constant or equal, the composite system cannot evolve.

Nevertheless, there may occur, as explained in 7. c) , an *evolution* which is *undetermined* when the separating wall is *mobile* and *adiabatic*. In this case –if there is inner dissipation in each of the subsystems– steady equilibriums can be obtained when the final temperatures of both are different. But we must point out that the temperatures *will generally vary*, even if they were identical to start with. If there is no inner dissipation, the system *will oscillate*: the U_c will not remain constant but will change between relative maximums and minimums and its entropy will do the same.

This *indetermination* occurs because, even when a steady equilibrium is obtained, all *virtual evolutions* of systems do not satisfy the general conditions:

$$dS = 0 \qquad d^2S < 0$$

thus, if this occurred, it would have to be:

$$T^{(1)} = T^{(2)}$$

which, generally speaking, does not happen. As we said earlier, this is a case of *indetermination*.

12. CONCLUSION.

From what has been analysed in this study we may conclude, by way of a summary, that a *composite system* obtains steady equilibrium if the following conditions are true:

- that it is *isolated* and that $U_p^{non\ addit}$ is *minimum*, i.e $dU_p^{non\ addit} = 0$

– that: $dS = 0$ and $d^2S < 0$, in any *virtual evolution*, in an environment where the position is of steady equilibrium.

Nonetheless, there may be some case of steady equilibrium that does not satisfy this last condition, like the one which was analysed above. We can say that the condition of *maximum entropy* is *sufficient* for *steadiness* but it is *not necessary* as a general rule and in all cases.

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