

## RESEARCH ARTICLE

# Entropy-Time Relationship in an Isochoric Adiabatic System

Francisco Ros\*

Institute of Medical Chemistry, Higher Council for Scientific Research, Madrid, Spain

\*Corresponding author: Francisco Ros, Institute of Medical Chemistry, Higher Council for Scientific Research, Madrid, Spain, Tel: +34915622900, E-mail: iqmr322@iqm.csic.es

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## Abstract

A quantitative entropy-time relationship has been concealed in thermodynamics by the unattainability of equation  $(\partial S/\partial V)_{T(p)} = S/V$  that would have allowed for an introduction of time by volume. The fundamental equation that connects the magnitudes entropy and time has been found for the first time by static thermodynamics:  $dS/S = dV_1/V_0 = k d\tau$ ,  $V_1$  internal volume. Internal volume is a genuine thermodynamic magnitude bound to the transforming energy of an isochoric adiabatic system. The energy differentiates by itself into heat and work while entropy points the weariness of the energy. Constant  $k$  also equals  $dT/T d\tau$  and is an individual characteristic for each isochoric adiabatic system in transformation. The constancy of  $k$  does not hold for a nonisochoric adiabatic system. In such a manner time is introduced in the frame of thermodynamical variables as a genuine magnitude and is properly connected to mechanics for the sake of volume. The theoretically deduced entropy-time differential equation is fully upheld empirically by Newton cooling law. It was found in connection with an a priori notion of thermodynamic equilibrium that irreversible heat capacity ( $C_{IR} = T\Delta S/\Delta T$ ) approaching thermodynamic equilibrium serves as an indicator for the equilibrium.  $C_{IR}$  is alike to statistical Boltzmann  $H$  in the approach to thermodynamic equilibrium, and the connection of  $H$  with temperature is given. The integrated entropy-time equation was modified by rotation of the coordinate axes to fulfill the necessary thermodynamical condition that pertinent irreversible heat ( $Q_{IR} = T\Delta S$ ) is less than ideal reversible heat ( $dQ = TdS$ ), what is not embodied in the primitive  $S$ - $\tau$  differential equation. This thermodynamically indispensable rotation gives rise in a natural manner to an otherwise unsubstantiated maximal entropy positively having a definite entropy-time maximum point at a finite time. The transformation of the  $S$ - $\tau$  function conveys a contraction of both entropy and time with respect to the reversible path, and is in agreement with the principle of minimal action.

**Keywords:** Irreversibility Thermodynamics; Entropy-time Equation; Maximal Entropy; Boltzmann  $H$ ; Thermophysics

## Introduction

The thermodynamical magnitude entropy has been recently used to determine other thermodynamical magnitudes in molecular solids [1-3]. This new methodology started up with experimental thermodynamical measurements, and the solid was depicted by a thermal oscillator that reproduced the vibrational energy and entropy of the solid. The potential energy of cohesion between molecules remained as an undetermined component of the total internal energy of the solid (vibrational in addition to the cohesion energy), and the cohesion energy was attained with the assistance of statistical mechanics and a variational method based on entropy rather than on internal energy. The usefulness of entropy here just rested on the null entropy of potential energy of cohesion as results from Planck's enunciation of third law of thermodynamics [3,4,5]. So the merely thermal entropy of a molecular solid was correlated with the thermal energy the solid by statistical mechanics, which permitted to obtain the desired cohesion potential energy from the total energy of the solid.

We have now been concerned in an antecedent and more complex feature of entropy. Entropy in a thermally isolated substance or thermodynamic system undergoing a change (heat  $Q = 0$ ) will have increased when the process has ceased reaching equilibrium, in conformity with second law of thermodynamics. In other words, the entropy of a thermally isolated body (adiabatic) increases when thermodynamical variables of state [*e.g.*  $f(U, T, Y) = 0$ ] change in a transformation.

Any stage in such adiabatic processes may be a state of "apparent" thermodynamic equilibrium if temperature and pressure (or generalized force  $Y$  for  $p$ ) are uniform in the system at a moment in the process. So the entropy will be a definite quantity along the process in agreement with the equation of state of the system. However, such ongoing intermediate states may not be of true equilibrium in thermodynamical sense. For instance, an adiabatic chemical reaction that would slowly enough take place is a well-known real case of perfect succession of equilibrium states in agreement with the equation of state for the reactive system. Hence the reaction also is a thermodynamically reversible process being as it is a continuous sequence of equilibrium states.

On the other hand, a process consisting of an unceasing succession of equilibrium states seems unnatural and nonsensical. Actually, such a chemical reaction is thermodynamically irreversible in strict sense because moves along with increasing entropy as is an adiabatic process for which irreversibility must be adhered according to second law. From the thermodynamical viewpoint such apparently reversible transformations may be called *pseudoreversible*, and they will be considered in the work in addition to normal irreversible processes. These often approach reversibility sufficiently well in practice [6].

## Scope of the Research and Attainments

Thermodynamic entropy, as distinguished from statistical entropy, is in general not defined during an irreversible process, but this may be described by an ideal, parallel reversible path having defined entropy. This concept has been adopted in this work. Thus a growing mathematical function theoretically derived should exist correlating entropy and time in a natural adiabatic process [ $S = f(\tau)$ ,  $dS/d\tau > 0$ ], and we have successfully searched for a general and mathematically explicit expression of such a function.

The matter of the relationship of entropy to time has recently been approached from a statistical point of view [7,8] differently from the purely thermodynamical treatment in the present research. Those statistical approaches do not provide a definite entropy-time correlation.

The present search has been undertaken for a system that is isochoric (*i.e.* at constant volume or, in general, not producing or receiving work) in addition to be adiabatic. "Isochoric adiabatic" stands for "thermodynamically isolated". The condition of the system be isochoric allowed in an exclusive manner for management of time in an unambiguous manner.

Time is classically introduced in thermodynamics as divisor in the two sides of a thermodynamical equation [4]. This brings about coefficients of flux as newly generated and sometimes awkward or meaningless quantities or brings about artificially predetermined

kinetics [9]. Such operation makes time to be a contingent magnitude. In contrast, we have found that time can be inserted into only one side of the appropriate equation. This represents a genuine and undependable introduction of time into the body of thermodynamics.

A reason that has concealed the introduction of time in a fundamental manner in thermodynamics is the unattainability of equation  $(\partial S/\partial V)_{T(p)} = S/V$  connecting the extensive magnitudes entropy and volume in basic equation  $dU = TdS - pdV$ . So the obvious connection of mechanical volume (space) with time by the way of velocity is blocked as to the passage to the entropy.

Figure 1 depicts the fundamental steps to the entropy-time relationship for the adiabatic system at constant volume. The key equation is differential equation (1) connecting entropy and volume. This equation has been theoretically deduced in the work, and exclusively using methodology of classical thermodynamics [4,5] and rigorous, logical physicomathematical reasoning.

$$\frac{dS}{S} = \frac{dV_1}{V_0} \tag{1}$$

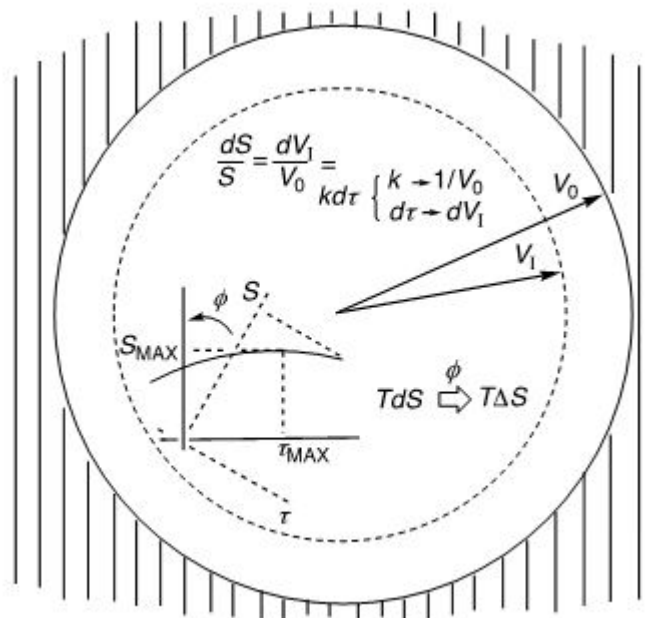


Figure 1: Sketch of the procedure to the differential and integrated entropy-time relationships

The concept of *internal volume* ( $V_1$ ), which is associated with the concept of *internal work*,  $dW_1 = pdV_1$ , has been used as necessary to counteract the actual constancy of volume in the process. By first law of thermodynamics the internal energy is constant in the process since the system is adiabatic and isochoric,  $dU = dQ - dW$  with  $dQ$  and  $dW$  equal to zero. It would thus appear that the law, which brings about a zero equality, cannot be used, at the same time that the detailed expression of the law is  $TdS - pdV = 0$  with  $dS$  actually greater than zero (by second law, irreversible process) and  $dV$  equal to zero, which results in an impossible inequality. Internal volume is therefore needed as a replacement of bulk volume.

Internal volume is not an artificial or heuristic concept but full of physical meaning. Thus, the actual production of entropy within the adiabatic system cannot be attributed to normal external heat ( $dQ = 0$ ) but to *internal heat*,  $dQ_1 = TdS$ , which was classically named “noncompensated heat” by Clausius about the development of second law [4, p. 139]. Internal heat in turn requires an equivalent amount of internal work since internal energy is constant. Internal volume therefore is a requisite of both first and second laws in the system.

Unconditioned equation  $dS/S = dV_1/V_1$ , analogous to (1), is not appropriate because does not take into account the constancy of volume in the system ( $V_0$ ). General equation  $dS/S = dV/V$  is valid to a nonisochoric adiabatic system. Instead of artificially manipulating these equations, eq. (1) singularly arose as a mathematical solution of the system of differential equations applicable to the isochoric adiabatic system. The correctness of the mathematical deduction leading to (1), which simultaneously refers to a constant volume and its differential volume, will be rigorously and exhaustively demonstrated below. Also, the uniqueness of this deduction in the framework of thermodynamical variables will be analyzed. Furthermore, the validity of modified equations to the system at merely constant internal energy ( $Q = W$ ) and to the just adiabatic system (nonisochoric,  $\Delta U = -W$ ), related to the isochoric adiabatic system, is pointed out in the work.

Straightforward introduction of time into eq. (1) by the right hand side of the equation gives a first order law for the velocity of increase in entropy ( $dS/d\tau = kS$ ,  $k$  for  $1/V_0$ ,  $d\tau$  for  $dV_1$ ). The replacement of internal volume by time in the entropy-volume equation is physically valid since the process considered takes place in time, and the replacement unfolds the natural relation between entropy and time. Time is the only pertinent and fundamental magnitude lacking in the frame of thermodynamical variables and the frame is not unsettled by the substitution of time since a fixed constant (as a first order velocity constant), not a variable parameter, is maintained upon the substitution ( $k$  for  $1/V_0$ ), what warrants the soundness of the substitution. The introduction of time will be justified in details in the discussion section.

In order to obtain empirical support for the theoretical bringing of time, experimental Newton cooling law concerning heat flux ( $dQ/d\tau = TdS/d\tau$ ) was examined as adapted to the thermodynamically isolated system. By a careful dimensional analysis this law converts into an equivalent expression of the entropy-time differential equation resulting from eq. (1) by the introduction of time, validating this last operation itself. As regards the constancy of the velocity parameter ( $k$ ) in the theoretical equation, conformity of the experimental law with the theoretical equation turns out complete when the number of variables in the thermodynamically isolated system is taken into consideration.

The matter of attainment of thermodynamic equilibrium in the system has been examined in the work, as a matter independent of time in the classical manner and previously to the integration of differential entropy-time equation since the integration limits are equilibrium points. It will be shown that irreversible heat capacity ( $C_{\text{IR}} = Q_{\text{IR}}/\Delta T = T\Delta S/\Delta T$ ) serves as an indicator for the thermodynamic equilibrium which complements a priori growth of the entropy to a maximal value. Irreversible heat capacity decreases in approaching equilibrium and is thus similar to statistical Boltzmann magnitude  $H$ . The consequent correlation of  $H$  with temperature will be given.

Equilibrium in natural thermodynamical systems is reached at a finite time according to empirical knowledge. However, by the integrated entropy-time function describing the reversible path of the process for the real irreversible path (necessarily irreversible according to second law as  $\Delta S > 0$ ), maximal entropy was asymptotic to time (see Figure 1). The primitive, nonintegrated entropy-time differential equation misses the indispensable condition of a diminished irreversible heat (second law, Clausius inequality,  $dQ_{\text{IR}} < TdS$  [4]), as such differential equation refers to infinitesimal, reversible changes in the entropy. Therefore, the integrated function was adjusted by simply an axes rotation to such unavoidable thermodynamical requirement, giving in this manner a mathematical function for the relation of entropy and time which is satisfactory as to the existence of a maximal entropy at a finite time (Figure 1).

The number of independent variables in the system is previously analyzed as is crucial in the deductions. Also, the pertinent assisting thermodynamical functions of variables are examined as an indispensable tool for the deductions, and the fundamental thermodynamic correlations between magnitudes which thereby arise are set forth. These sections in the article, previous to the deduction of the entropy-time relationship, are necessary for appropriate definitions to the isochoric adiabatic system.

A nomenclature for magnitudes and symbols used in the work is given in Table 1.

$A$	Magnitude action (work $\times$ time)
$C$	Heat capacity
$C_{IR}$	Irreversible heat capacity (heat capacity to heat irreversibly developed)
$C_V$	Heat capacity at constant volume
$F$	Assisting free-energy function
$\phi$	$\text{arccot}(dS/dT)$ ( $\phi$ degree of reversibility)
$G$	Assisting free-enthalpy function
$H$	Assisting enthalpy function; statistical magnitude Boltzmann $H$
$k$	Velocity constant of entropy-time equation
$k_B$	Boltzmann constant
$k_N$	Coefficient of Newton cooling law
$p$	Pressure
$Q$	Heat
$Q_I$	Internal heat
$Q_{IR}$	Irreversible heat (heat irreversibly developed)
$Q_T$	Heat of transfer
$S$	Entropy
$T$	Absolute temperature
$T_E$	Exterior temperature
$\tau$	Time
$U$	Internal energy (total energy content); assisting internal-energy function
$V$	Volume
$V_I$	Internal volume
$V_0$	Volume of isochoric system (constant volume)
$W$	Work
$W_I$	Internal work
$Y$	Generalized intensive magnitude (generalized force)
$X$	Generalized displacement
$X_I$	Generalized internal displacement

Table 1: Nomenclature of magnitudes and symbols

### Basic equations for the reversible and irreversible processes in the isochoric adiabatic system

Since the system is adiabatic and nonworking ( $Q = 0, W = 0$ ) the principle of equivalence  $\Delta U = Q - W$  (general expression of first law) lets only know that the change in internal energy for the transformation is null. Nevertheless, this equation becomes manageable with internal heat and internal work as replacements [eq. (2)]. The definition and physical soundness of internal heat and work have been set forth in the preceding section (Scope of the research and attainments).

$$Q_I = W_I \tag{2}$$

As a work, internal work can be expressed by generalized force  $Y$  and generalized internal displacement  $X_I$  for a detailed expression of first law, eq. (3) ( $pdV_I$  in particular). Magnitude  $Y$  refers to an actual force in the system, in particular the applicable external mechanical pressure ( $p > 0$ ). Although internal work may be evaluated, is not profitable work. Real useful work can however be produced within the thermodynamically isolated enclosure considered as in the discharge of an electrical battery in an isolated room. However, when the process stops by itself no serviceability of the work remains, this useful energy being fully converted into internal heat and entropy [eq. (2), (3)]. It is in this sense that work is here meant.

$$TdS = YdX_I \tag{3}$$

The total internal heat and work for the process can be expressed as in eq. (4) where  $T_I$  is the initial temperature and  $Y_I$  the initial value of the force. This equation refers to the process as fully irreversible. It is underlined regarding the character of the work that internal displacement  $X_I$  may be an unmeasurable quantity, as  $V_I$  is.

$$T_1 \Delta S = Y_1 \Delta X_1 \quad (4)$$

As signified in eq. (4), quantity  $Q_1$  and  $W_1$  represent the minimal, irreversible internal heat and work, as compared with a reversible path. Figure 2 shows a temperature-entropy diagram with indication of the irreversible heat. The actual irreversible heat will depend on the specific degree of irreversibility of the process (drawn up area in the figure).

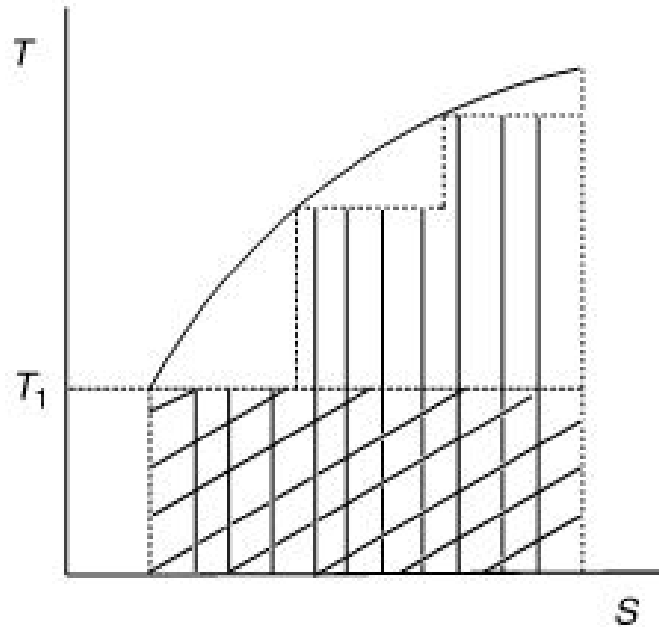


Figure 2: Irreversible heat (highlighted areas)

The reference temperature for the amount of irreversible heat is the low temperature. Thus by second law, heat that is transferred in an irreversible manner cannot be greater than the reversible heat, *i.e.*  $dQ = TdS$ ,  $dQ_{IR} < TdS$  [4]. This holds even though heat flux in the present system is actually toward high temperature, as it will be shown below. As regards irreversible internal work the reference is similarly the initial low pressure, which is in contrast with the *final* low pressure as reference for the amount of work in a normal irreversible expansion (it is shown below that  $p$  and  $V_1$  increase in the transformation of the present system).

The concept of minimal irreversible internal heat, as depicted in Figure 2, is crucial in the isochoric adiabatic system as it will shown that the maximum of the entropy-time curve arises because of this condition.

### Variables in the system. Degree of freedom

The composition or the set of the system is not allowed for. A change in aggregation of matter or in chemical composition does not give rise to an independent variable as mass is constant. In a similar manner, a change in the setting of a system (*e.g.* in an electrical device) is brought about by conversion of internal work into internal heat, which are not independent from each other since internal energy is constant [*i.e.* eq. (2)], and thus the adjustment of the set does not demand an additional independent variable. As regards nonuniformity of temperature or pressure (or generalized force  $Y$ ) in the system, a mean value may be used.

The state of the thermodynamically isolated system can thus be defined with two thermodynamical variables, in the same manner that to a single substance [*e.g.*  $f(U, T, Y) = 0$ , internal volume playing the role of normal volume  $V$ ], and such two variables are in turn not independent from each other since internal energy is constant for the system. Therefore, just one variable is sufficient to specify the state of the system at any moment. This is of mathematical relevance according to the way that the use of partial derivatives is not necessary, simple derivatives being sufficient for the mathematical treatment of the system.

Beyond this point, the degree of freedom of the system (number of independent variables) is in reality zero and not one since internal volume is not a true physical or thermodynamic parameter as is unobservable. In reality,  $dU = TdS - pdV$ , with  $dU = 0$  and  $dV = 0$ , hence  $dS = 0$ , which points the nought degree of freedom. This lack of degrees of freedom is most important for the relevance of experimental Newton cooling law for the system, as it will be shown below.

We will refer to chemical systems (otherwise called mechanical) in the equations below ( $Y \equiv p$ ;  $X \equiv V, V_1$ ).

### Assisting thermodynamical functions for the system. Maxwell equation

Internal-energy function  $U = TS - pV_1$  is incongruent in its nature of a variable function for the system because of the actual constancy of internal energy. Then variable  $U$  is made it to be a constant having an arbitrary value that is set to zero for easiness [eq. (5)]. This functional expression adequately connects the variables for the system in a formal, operative manner.

$$TS - pV_1 = 0 \quad (5)$$

Enthalpy and free energy are defined by eq. (6) and (7), fittingly to (5). Free enthalpy,  $G = pV_1 - TS$ , is not of assistance for the system as is a redundancy of the internal-energy function ( $U = TS - pV_1$ ) that is useless.

$$H = pV_1 \quad (6)$$

$$F = -TS \quad (7)$$

The assisting functions (5) -(7) are pertinent to a system that undergoes a change merely at constant internal energy, *i.e.*  $dU = 0 = TdS - pdV$ , setting bulk  $V$  in place of  $V_1$ . This latter adapted form of the basic equation [(3)] is also appropriate for a thermally isolated system (adiabatic system) doing work despite internal energy is not constant in this case. Thus, in a spontaneous irreversible adiabatic process entropy increases by second law. The internal heat concomitant to this increase in entropy is produced at the expense of internal energy, *i.e.*  $dQ_1 = TdS = -dU$ , which results in expression  $TdS - pdV = 0$  for the basic equation as the formal increase in  $dU$  becomes offset, and the corresponding assisting function therefore is  $TS - pV = 0$ .

Differentiation of eq. (5) -(7) and use of equality (3) ( $TdS = pV_1$ ) give differential (8)-(10).

$$SdT - V_1 dp = 0 \quad (8)$$

$$dH = V_1 dp + TdS \quad (9)$$

$$dF = -SdT - pdV_1 \quad (10)$$

Term  $SdT$  and  $V_1 dp$  appearing in eq. (8) are second terms in the differentials of nominal heat  $TS$  ( $dTS = TdS + SdT$ ) and nominal internal work  $pV_1$  ( $dpV_1 = pdV_1 + V_1 dp$ ). Eq. (8) is a necessary condition for the system concerning those terms, in the same manner that it is true for the actual constituents of internal heat  $dQ_1$  ( $TdS$ ) and internal work  $dW_1$  ( $pdV_1$ ) according to basic (3) ( $TdS - pdV_1 = 0$ ). In term  $SdT$  the entropy may be considered an equivalent of heat capacity, taking  $SdT$  for  $dQ_1$  ( $C = dQ_1/dT \equiv S$ ). Similarly internal volume in  $V_1 dp$  may be considered a coefficient of pressure regarding work, taking  $dW_1 = V_1 dp$  rather than its actual definition  $dW_1 = pdV_1$ . It will be disclosed in a below section that these appraisals are entirely correct.

From either eq. (9) or (10), eq. (11) comes out taking into account that the former are exact differentials [4] and that their coefficients are functions of only one variable as pointed out in the preceding section, what allows for derivatives to be total rather than partial at (11). Eq. (3) ( $TdS - pdV_1 = 0$ ) and (8) do not give rise to a Maxwell equation such as (11) (as it contrarily is the case when  $dU$

and  $dG$  are not null [4]) because such (3) and (8) are differentials equal to zero which instead results in a zero equality instead of an explicit equation like (11). Eq. (11) stands for the Maxwell equation for the present thermodynamically isolated system. It also holds for a system at constant internal energy involving external heat as well as for a working adiabatic system by replacement of  $V_1$  by  $V$  (systems above mentioned).

$$\frac{dS}{dV_1} = \frac{dp}{dT} \quad (11)$$

### Thermodynamic correlations

Temperature increases on a transformation of the thermodynamically isolated system because heat, as internal heat, is gained by the system, and heat capacity at constant volume is a positive quantity by principle, notwithstanding that internal heat rather than normal heat is concerned, *i.e.*  $dT = dQ_1/C_v = TdS/C_v > 0$  with  $dS$  and  $C_v > 0$ . For a substance, heat capacity  $C_v$  is always positive [5]. The positive character of  $C_v$  in the system is independent of the flux of internal heat to actually higher temperatures, which in turn does not contradict the principle that heat fluxes to lower temperatures as internal heat and not external heat is concerned. It will be independently shown in a below section that the increase in temperature in the system follows the inherent increase in entropy.

For a transformation at constant internal energy whereby external heat is transferred from or to the system, the direction of a temperature change ensues the sign of  $dS$  ( $dT = TdS/C$ ,  $dS$  greater or less than 0,  $C > 0$ ). For a working adiabatic system, temperature decreases as entropy increases. Thus, it follows an increase in entropy that heat is lost by the system in an internal manner (as the system is thermally isolated) and this loss of heat from the internal energy reduces the temperature of system as owed to the energy. This will be further shown in a section below.

By consideration of precedent equations the following correlations for the isochoric adiabatic system come out. Internal volume increases on the transformation according to eq. (3), *i.e.*  $TdS = pdV_1$  with  $dS$  and external pressure  $p > 0$ . Then gradient  $dV_1/dT$  is positive as  $dT$  is. Gradient  $dp/dT$  is positive according to eq. (12), which results from elimination of  $dS/dV_1$  from (3) and (11), so pressure increases in the transformation as temperature does. Gradient  $dV_1/dp$  is positive for the thermal transformation considered ( $dV_1$  and  $dp > 0$ ). This is in contrast with the isothermal compressibility of a substance which is negative, but the conditions here considered are not isothermal; moreover, it should be recalled that internal volume is not just bulk volume.

$$\frac{dp}{dT} = \frac{p}{T} \quad (12)$$

Preceding correlations may be extended to nonchemical systems. In reference to an electrical system the electric charge is unloaded as entropy increases in the thermodynamically isolated system, *i.e.*  $TdS = -\epsilon dq$  [suited basic (3) with the applicable sign for electrical work] with  $dS > 0$ , hence  $dq < 0$ . At the same time, electromotive force decreases, *i.e.*  $SdT + qd\epsilon = 0$  [electrical analogue of (8)] with  $dT > 0$ , hence  $d\epsilon < 0$ .

### Deduction of the differential entropy-time equation

The generic correlation between entropy and internal volume for the isochoric adiabatic system, eq. (13), rises by elimination of derivative  $dp/dT$  from auxiliary differential equation (8) and Maxwell equation (11). It may be noted that basic equation (3) does not directly take part in the rising of (13), what is in contrast with the pressure-temperature relationship for the system as above shown.

$$\frac{dS}{S} = \frac{dV_1}{V_1} \quad (13)$$



Eq. (13) is also applicable to a nonadiabatic system at constant internal energy ( $dQ \neq 0$ ,  $TdS - pdV = 0$ ) by substitution of real volume for internal volume, *i.e.* eq. (14). This latter general equation is also valid to a merely adiabatic system ( $dQ = 0$ ,  $dU = -pdV$ ) on assumption that the internal heat in the transformation is produced at the expense of internal energy as mentioned in the preceding section. In an irreversible, spontaneous adiabatic transformation the concomitant increase in entropy conveys an expansion like the free expansion of a thermally isolated gas. Otherwise, a decrease of the entropy with a contraction will occur in nonspontaneous adiabatic transformations, which are not subject to second law as are not spontaneous (spontaneity, or nonconcurrency of promotive external forces is a requisite for second law [4]). In conclusion, eq. (14) is applicable to systems not having the restriction of volume constancy.

$$\frac{dS}{S} = \frac{dV}{V} \quad (14)$$

For any of the circumstances for which eq. (13) and (14) are valid, time can be brought about in a dimensionally correct manner by substituting for the right hand side of the equations with a time differential multiplied by a frequency that may in general be variable ( $dV_1/V_1 = x d\tau = dS/S$ ). However, with entropy as any function of time the introduction of time is not consolidated, yet dimensionally correct. Moreover, the operation, which is ambiguous as to the character of the frequency and of the entropy-time function, does not warrant the insertion of time as a fundamental magnitude in the thermodynamical frame of variables. This difficulty can be overcome by means of the actual constancy of volume for the isochoric adiabatic system as it is shown in the following.

*Deduction of the differential entropy-time equation by means of the specific assisting thermodynamical function for the isochoric system; mathematical proof for the differential equation*

Putting basic equation (3) ( $TdS = pdV$ ) to the condition of constant volume, eq. (15) results. Since volume has been fixed, differential  $dV_0$  is zero. Differential  $dS$  is therefore zero as well. This may taken to mean that variable  $S$  has a constant value although remaining an indeterminate value. This indeterminacy of  $S$  is congruent with the result obtained by differentiating the specific assisting thermodynamical function for constant volume, eq. (16), and then using (15). Resulting (17) is crucial for solving the system of differential equations, and points out that gradient  $dp/dT$  is a linear function of  $S$ . By (17) the aboved-mentioned indeterminacy of  $S$  is resolved.

$$TdS = pdV_0 \quad (15)$$

$$TS = pV_0 \quad (16)$$

$$\frac{dp}{dT} = \frac{S}{V_0} \quad (17)$$

Eq. (17) can be obtained in an unmistakable alternative way wherein  $dS$  is not zero in agreement with the real situation ( $dS > 0$ ). Since the system is isochoric and work is so not performed, first law (with  $dU$  and  $pdV$  equal to zero) can be expressed as eq. (18). In this manner,  $dU^*$  refers to an apparent increase in internal energy, and is equivalent to the internal heat produced ( $dU^* = dQ_1$ ). This increased special internal energy is in turn employed to the work internally produced,  $dU^* = -dW_1$ , which leaves constant the true internal energy as it is. This substitution of  $dU^*$  for zero permits the management of first law for the system esteeming both the actual constancy of volume and the entropy increase. The applicable assisting thermodynamical function is in this case eq. (19), which relates to all concerned quantities and stands for an appropriate assisting function for the system. Differentiation of this equation and subtraction of (18) gives back crucial eq. (17) as it was pursued.

$$dU^* = TdS \quad (18)$$

$$U^* = TS - pV_0 \quad (19)$$

Beyond the preceding physical interpretation and from a purely mathematical viewpoint, the use of an auxiliary variable ( $U^*$ ) leaves no doubt about the correctness of crucial differential equation (17), which permits to solve the system of differential equations and on which we proceed in the following.

With the previous idea of obtaining in a direct manner the entropy-volume differential equation for the condition of constant volume ( $dS/S = dV_1/V_0$ ), working up in the usual manner eq. (15) with the particular assisting enthalpy function ( $H = pV_0$ ) or the corresponding free-energy function gives equation  $dS/S = dV_0/V_0$  that is however void ( $dV_0 = 0$ ).

Instead, eq. (17) is equated to Maxwell equation (11) ( $dp/dT = dS/dV_1$ ), which is generally valid regardless of the particular  $V_0$  value and in which  $dV_1$  is not null as above. This operation results in equation  $dS/S = dV_1/V_0$  [(1)] that expresses the key relationship between entropy and volume for the isochoric adiabatic system and by means of which magnitude time can be introduced in an unambiguous manner.

The interpretation to key eq. (1) is as follows. In auxiliary eq. (8) ( $dp/dT = S/V_1$ ), gradient  $dp/dT$  refers to all values of internal volume and thus corresponds to an ensemble of  $S$ - $V_1$  values, *i.e.*  $dp/dT = f(S, V_1)$ . On the other hand in eq. (17) ( $dp/dT = S/V_0$ ) the gradient refers to the particular  $V_0$  value and to a single  $S$ - $V_1$  correlation, *i.e.*  $(dp/dT)_0 = f(S, V_0)$ . Upon the indicated equalization using Maxwell equation, resulting eq. (1) ( $dS/S = dV_1/V_0$ ) provides the analytical solution to the  $S$ - $V_1$  correlation at the  $V_0$  value, *i.e.*  $f_0(S, V_1)$  as the integral of (1).

Finally, in a dimensionally permitted manner the adimensional right hand side of eq. (1) ( $dS/S = dV_1/V_0$ ) is equated to an elemental time differential multiplied by a frequency that for homogeneity with  $1/V_0$  is set as constant [eq. (20)]. This substitution of time gives rise to the differential entropy-time equation for the isochoric adiabatic system, eq. (21), by means of (1). In (21), quantity  $k$  stands for a constant, independent of any variable in the system being as it is a replacement of  $1/V_0$ . Constant  $k$  is a characteristic of each thermodynamically isolated process and has the dimension of a first order velocity constant [in (21)] or of a frequency ( $\tau^{-1}$ ). The dimensional substitution of time for volume rendering entropy equation (21) is most consistent with the natural relation between entropy and time in second law [4,5].

$$\frac{dV}{V_0} = kd\tau \quad (20)$$

$$\frac{dS}{S} = kd\tau \quad (21)$$

The introduction of time in generic eq. (13) ( $dS/S = dV_1/V_1$ ) rather than in specific (1) ( $dS/S = dV_1/V_0$ ) does not permit to fix quantity  $k$  as constant since  $V_1$  is variable ( $k$  replaces  $1/V_1$ ,  $dS/S = x d\tau$ ). Thus magnitude time remains unanchored in the frame of thermodynamic magnitudes contrarily to its introduction by the specific equation for the isochoric system.

The relationship between internal volume and time is linear as ensues eq. (20) while the relationship by unspecific  $dV_1/V_1 = x d\tau$  is at best exponential when a chimerical constant value is set for truly variable  $x$  ( $dV_1/V_1 = kd\tau$ ). The linear  $V_1$ - $\tau$  function is a secant to the exponential  $V_1$ - $\tau$  function. So time takes a longer path in the latter unspecific function and drifts from the immediate straight path provided by the specific function. This immediate path is consubstantial with the nature of time. It also accounts for the physical appropriateness of the introduction of time in thermodynamics by means of eq. (1).

The nature of the introduction of time is further discussed in the corresponding subsection of the following section.

### Discussion on the differential entropy-time equation

*Exclusiveness of entropy-volume equation (1) ( $dS/S = dV_f/V_0$ ) and (13) ( $dS/S = dV_f/V_f$ )*

Differential  $V_f dp$ , a term in  $dpV_f$ , can in a correct manner (as validated below) be taken as a substitute for work  $p dV_f$  in the differential equations, which brings about further correlations among the variables  $T, S, p$  and  $V_f$  as well as  $V_0$  in addition to the correlations above indicated. However, these extended correlations do not include neither the key entropy-volume equation for the system [ $dS/S = dV_f/V_0$  (1)] nor generic (13) ( $dS/S = dV_f/V_f$ ) that sustain the entropy-time equation for the system, which reveals the exclusiveness of the  $S-V_f$  equations and the unambiguity in their deduction.

*Validation of the exchange of work term  $p dV_f$  by flux term  $V_f dp$  for the system*

In the manner of such exchange of  $p dV_f$  by  $V_f dp$  and for the condition of constant volume, basic equation (3) ( $TdS = p dV_f$ ) converts into (22). Dividing this equation by  $dT$ , eq. (23) results where the so-called heat of transfer  $Q_T$  stands for quantity  $-T^2 dS/dT$  (by multiplying both terms of the middle fraction by  $T$ ). Eq. (23) concerning  $Q_T$  for a thermodynamically isolated system has been independently derived by a different method [4, p. 415] that does not involve the exchange of  $p dV_0$  by  $V_0 dp$ , therefore validating the exchange as this yields a correct equation. Moreover, an explicit expression for  $Q_T$ , as indicated, is provided by the present method contrarily to the classical method.

$$T dS = V_0 dp \tag{22}$$

$$\frac{dp}{dT} = \frac{T}{V_0} \frac{dS}{dT} \equiv -\frac{Q_T}{V_0 T} \tag{23}$$

*Extended thermodynamic correlations for the system*

For variable volume ( $V_f$ ), basic equation (3) converts into (24) by substitution of work for  $V_f dp$ . This latter equation together with the assisting internal-energy function [(5)] and Maxwell equation [(11)]—these latter ones holding in regard to exchanged (24)—produce (25)-(27) by the usual methodology in precedent sections. Eq. (25)-(27) correspond to (8), (12) and (13), respectively, which arise from the regular, nonexchanged basic equation and remarkably do not comprise the generic entropy-volume equation (13).

$$T dS = V_f dp \tag{24}$$

$$\frac{dV_f}{dT} = \frac{S}{p} \tag{25}$$

$$\frac{dV_f}{dT} = \frac{V_f}{T} \tag{26}$$

$$\frac{dS}{S} = \frac{dp}{p} \tag{27}$$

Similarly, eq. (22) with Maxwell equation gives (28) that is analogous to specific entropy-volume eq. (1) ( $dS/S = dV_f/V_0$ ), but refers to temperature not containing the entropy.

$$\frac{dT}{T} = \frac{dV}{V_0} \tag{28}$$

The preceding deductions not yielding the entropy-volume relations for the system [eq. (1) and (13)] manifest the exclusiveness of the deductions presented in the preceding section for these relations.

### Entropy-temperature relationship for the system

By correlations in the sets of equations departing from  $TdS = pdV_1$  and  $TdS = V_1dp$  the equality of the two terms of the differential of nominal heat  $TS$  ( $dTS$ ) or of nominal work  $pV_1$  ( $dpV_1$ ) comes out, which was put forward in a previous section. Thus eliminating volume between (13) ( $dS/S = dV_1/V_1$ ) and (26) gives (29), and eliminating entropy between (13) and (27) gives (30). These correlations are valid since the sets form an interrelated whole.

$$TdS = SdT \quad (29)$$

$$pdV_1 = V_1dp \quad (30)$$

Eq. (29) remarkably shows that entropy is equal to heat capacity in the thermodynamically isolated system ( $C = dQ_1/dT = TdS/dT = S$ ) [6]. Moreover, eq. (29) is important as establishes the relationship of entropy to temperature for the system, and will be used in discussions and deductions in subsequent sections.

### Nonisochoric adiabatic system

Equality (29) and (30) are not restricted to the isochoric adiabatic system but are valid to a nonadiabatic system ( $dQ \neq 0$ ) at constant internal energy ( $dU = 0$ , with changing bulk  $V$ ) since all equations for the former system are applicable to the latter system by replacing internal volume by volume and minding that entropy relates to external heat rather than to internal heat.

However, for a system no more than adiabatic (nonisochoric) such equalities are the opposite, *i.e.* (31) and (32). Eq. (31) comes out eliminating volume from (14) ( $dS/S = dV/V$ , applicable to the merely adiabatic system as previously indicated) and negative (33), and eq. (32) similarly results from general pressure-temperature relationship (12) ( $dp/p = dT/T$ ) and again (33).

$$\frac{dS}{S} = -\frac{dT}{T} \quad (31)$$

$$\frac{dV}{V} = -\frac{dp}{p} \quad (32)$$

$$\frac{dV}{V} = -\frac{dT}{T} \quad (33)$$

Negative (33) arises from the exchange of term  $pdV$  with  $Vdp$  concerning the merely adiabatic system wherefore the applicable basic equation and assisting function are  $TdS + Vdp = 0$  and  $TS + pV = 0$  in contrast with the isochoric adiabatic system (with a minus sign) whereas the applicable Maxwell equation is (11) as usual. The change of sign in the former equations renders the correct temperature correlation [(31)] and correct compressibility [(32)] for the nonisochoric adiabatic system, *i.e.* a decrease in temperature and pressure on an expansion with an increased entropy as in an adiabatic free expansion of a gas. Moreover, the exchange of  $pdV$  with  $-Vdp$  rather than with  $Vdp$ , which gives rise to  $TdS + Vdp = 0$ , is logical as this equation is just the null differential general enthalpy, *i.e.*  $dH = d(U + pV) = TdS + Vdp = 0$  ( $dU = TdS - pdV = 0$ ) [4], which is consistent with the actual null heat in the adiabatic system ( $dQ = 0$ ) as enthalpy refers to nominal heat  $TS$  ( $H = U + pV \equiv TS$ ).

## Nature of the introduction of time

The following arguments account for the introduction of time by eq. (1) and (20) ( $dS/S = dV_1/V_0 = kd$ ).

1. The existence of a physical relation between entropy and time is implicit in Clausius inequality in second law as applied to an irreversible adiabatic transformation since the sign of the change in entropy becomes predetermined for a natural transformation that takes place in time [4,10]. Such a relation is also implied in Prigogine theorem concerning the rhythm of production of entropy for a stationary system [4]. Also, time is implied in Boltzmann  $H$  theorem with regard to the time for reaching equilibrium ( $dH/d$ ), statistical magnitude  $H$  being closely connected with entropy [4]. The natural relation of entropy to time should be expressible in terms of an explicit mathematical function of theoretical nature.

2. Time has been brought about in this work by means of the volume right hand side of entropy-volume equation (1) ( $dS/S = dV_1/V_0$ ). Ahead of this, a relationship of a primitive character between volume and time is logical since volume represents a length or a spatial displacement, *i.e.* a volume-time relationship is a space-time relationship. By way of contrast, a relationship to time would in this context be inconsistent for temperature or pressure as these represent forces and are thermodynamically intensive magnitudes in contrast with volume and time. Moreover, from a formal viewpoint the correlation of volume and time by  $dV_1/V_0 = kd\tau$  [eq. (20)] is correct since represents a regular mechanical kinetics. The dimensional introduction of time by this equation ahead rests on the natural relationship of entropy to time.

3. Velocity laws of zero order [like  $dV_1/V_0 = kd\tau$  (20)] actually take place in nature, *e.g.* in chemical kinetics [11, p. 13]. In these real processes the property considered (here  $V_1$ ) is not a factor for the velocity but this is directed by an internal factor. Hence a zero-order law is most consistent with the internal character of the volume in eq. (20).

4. Because of the proportional nature of the relationship between internal volume and time the substitution of time is equivalent to a change of units with respect to internal volume, what does not unsettle the framework of thermodynamical variables.

5. The replacement of internal volume by time repairs the frame of experimental thermodynamic parameters since internal volume is not a true parameter yet time is. This restitution is demanded by entropy ( $dS/S = dV_1/V_0$ ), giving back complete the frame of paramers. Time becomes a genuine physical magnitude in the isochoric body.

## Empirical proof of the theoretical differential entropy-time equation by means of Newton cooling law. Definition of the velocity constant of the equation

In considering this law,  $dQ/d\tau = -k_N(T - T_E)$ , with regard to the thermodynamically isolated system it is first pointed out that the difference of temperature of the body undergoing cooling with respect to the external temperature ( $T_E$ ) is the driving force for the transfer of normal external heat ( $T - T_E > 0$ ) whereas internal heat is produced against high temperature in the thermodynamically isolated system, *i.e.*  $T - T_E > \Delta T$  in the system; for the thermodynamically isolated system in evolution, such difference of temperatures is thus taken for a finite increment of temperature occurring at any stage in the evolution from an arbitrary initial point. In addition, the heat of cooling referred to in the law ( $dQ < 0$ ) is taken for the internal heat in the system ( $dQ \equiv -dQ_1 = -TdS$ ). Those two considerations render eq. (34) to the system ( $\Delta T > 0$  as shown in a previous section, note that the minus sign in the law is here offset).

$$T \frac{dS}{d\tau} = k_N \Delta T \quad (34)$$

Eq. (34) in the form of  $dS/d\tau = k_N \Delta T/T$  may compared with theoretical equation (21) ( $dS/d\tau = kS$ ). As a matter of fact, law constant  $k_N$  is not constant in a specific cooling system but for an experimental approximation, and stands for no more than a phenomenological

coefficient whereas  $k$  in the theoretical equation is truly constant. Non-constant  $k_N$  is considered dependent of one variable as it was already discussed above for the thermodynamically isolated system, and in particular the temperature may be considered the required variable for  $k_N$ .

The dimensions of  $k_N$  are entropy divided by time, and  $k_N$  can be expressed as a fraction of an actual entropy value to the corresponding time in the evolution multiplied by an adimensional variable, *i.e.*  $k_N = xS/\tau$ . Independent variable  $x$  is indispensable for a match of actual quantities to  $k_N$ , *i.e.* a trivial dimensional setting is not sufficient even though  $k_N$  itself is variable.

In an alternative way the relationship of  $k_N$  to entropy and time can be disclosed recalling the coincidence of heat capacity and entropy for the system. Thus using eq. (29) ( $TdS = SdT$ ) in (34), which results in  $k_N = SdT/\Delta Td\tau$ , and then permuting differential and increment symbols in a dimensional manner results in  $k_N = yS/\Delta\tau$  in which  $y$  stands for an indeterminate finite quotient of infinitesimal quantities, *i.e.*  $y = \delta/\delta'$  with  $\delta = dT/\Delta T$  and  $\delta' = d\tau/\Delta\tau$ . So the latter expression for  $k_N$  in terms of entropy and time is equivalent to previous  $k_N = xS/\tau$ , with either  $y$  or  $x$  as variables.

Setting back the new expression for  $k_N$  in (34) gives (35). This is comparable with entropy-time equation (21) ( $dS/S = kd\tau$ ) to which is equivalent in meaning ( $k = y\Delta T/T\Delta\tau$ ). Since (35) arises from experimental Newton law, it provides empirical support to the theoretical entropy-time equation. More fundamentally, it dissipates any arbitrariness in the introduction of time itself in the frame of thermodynamic magnitudes by the methodology in this work. Nevertheless, the constancy of  $k$  as derived from Newton law remains a question, which is settled below.

$$\frac{dS}{S} = y \frac{1}{T} \frac{\Delta T}{\Delta\tau} d\tau \quad (35)$$

By eq. (36) the velocity constant of the entropy-time equation is the gradient of temperature with respect to time per unit of temperature value [variable  $y$  in (35) cancels in passing to (36) by the change of increments to differentials]. This expression of  $k$  can also be obtained directly equating previous eq. (21) and (29).

$$k = \frac{1}{T} \frac{dT}{d\tau} \quad (36)$$

The relation of the velocity constant to Newton law constant is given by eq. (37), as it ensues equations above. This equation does not precludes the constancy of  $k$ , as factor  $k_N$  is variable (as above pointed out) like factor  $\Delta T/TS$ . Nevertheless, neither (37) nor (35) [with  $k \equiv y\Delta T/T\Delta\tau$ ] positively establish the constancy of  $k$  when derived from experimental Newton law, while it is theoretically constant.

$$k = \frac{\Delta T}{TS} k_N \quad (37)$$

For a full match of Newton law to the entropy-time equation it is necessary to consider the actual constancy of volume for the isochoric adiabatic system in adapting the law to the system. Internal volume is here not pertinent, and the unchangeability of volume is a point that is not embodied in Newton law, but is to be taken into account in fitting the law to the system. The true degree of freedom of the system concerning variables is zero because of the physical unobservability of internal volume, as pointed out in a precedent section. For reason of the nought degree of freedom to the system, variable  $k_N$  in the law becomes a constant for the system. Remaining variable factor  $\Delta T/TS$  in eq. (37) here figures a constant in respect to the isochoric system (no independent variable at all), hence  $k$  is a constant.

The constancy of  $k$ , as results from the nought degree of freedom, can be further justified. Thus, differential  $d\tau$  in eq. (36) is accordingly taken as a constant infinitesimal quantity rather than it be a variable differential. As concerns  $dT/T$  in this equation, the dimensional

use of first Wien law,  $\lambda T = \text{const}$  (with wavelength  $\lambda$  in the role of condensed volume  $V$ ), brings about expression  $\Delta T/T \sim \Delta\lambda_0/\lambda_0$  making up the requirement of volume constancy ( $V_0$ ) [developing  $(\lambda + \Delta\lambda)(T + \Delta T) = \text{const}$ , then setting  $\lambda_0$ ]. Expression  $\Delta T/T \sim \Delta\lambda_0/\lambda_0$  indicates that  $dT/T$  in (36) figures a constant like  $d\tau$  has been taken to be, and  $k$  is hence a constant. This reasoning alternatively demonstrates the unchangeability of the velocity constant in the entropy-time equation for a particular isochoric adiabatic process

### Thermodynamic equilibrium as integration limit for the differential entropy-time equation

With the purpose of obtaining an insight to the a priori, indefinite thermodynamical notion that as a consequence of the growth of entropy in an irreversible thermodynamically isolated transformation the equilibrium is reached when entropy is maximal [4,5], it was used the entropy-temperature correlation for the system. The examination was also undertaken as a purely thermodynamical complement to the statistical enunciation that maximal entropy corresponds to maximal probability. The starting and end stages in the process of the isochoric adiabatic system represent points of thermodynamic equilibrium which are the limits for the integration of the differential entropy-time equation, presented in the following section.

The correlation of temperature with entropy is linear as follows integration of eq. (29) ( $dT/T = dS/S$ , Figure 3). For a fully irreversible transformation and with reference to the figure, heat capacity is expressed by  $C_{\text{IR}} = Q_{\text{IR}}/\Delta T = T_1(S_2 - S_1)/(T_2 - T_1)$ , taking into account the minimal irreversible heat indicated in a previous section (Figure 2). Also, it is  $C_{\text{IR}} = T_1 \cot\phi$ , and in these terms the initial entropy is  $S_1 = T_1 \cot\phi - a$ , where  $a$  is the intercept of  $T$ - $S$  line at  $S$  axis. Thus  $S_1$  is less than  $C_{\text{IR}}$  by quantity  $a$ , i.e.  $S_1 = C_{\text{IR}} - a$ . In order to make up the equality of entropy and heat capacity at equilibrium [previously pointed out, eq. (29)], quantity  $a$  is to vanish at the equilibrium.

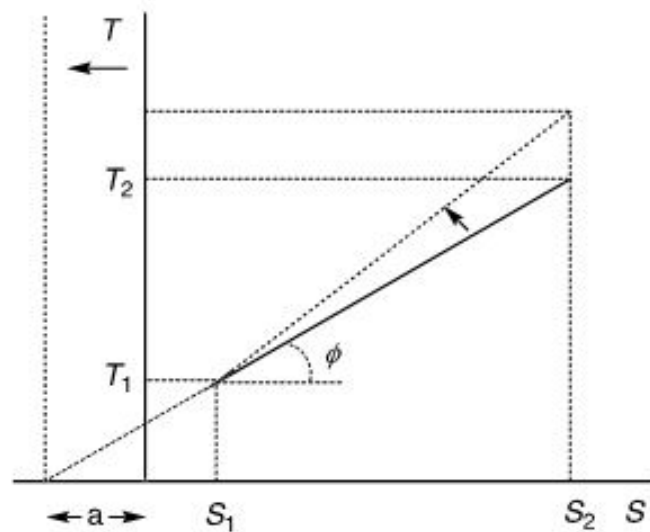


Figure 3: Transformations for entropy and heat capacity in an isochoric adiabatic system ( $C_{\text{IR}} = T_1 \Delta S / \Delta T$ )

The annulment of quantity  $a$  can be done on Figure 3 by a translation of axes to the intercept of  $T$ - $S$  line, which conveys an enlargement of  $S_2$  consistently with the entropy growth in the transformation while the slope and heat capacity are not altered. Otherwise line  $T$ - $S$  can be rotated around point  $(S_1, T_1)$  to set the new intercept at the origin (rotation betoken by slanted arrow), not altering distance  $S_1 S_2$  but increasing  $T_1 T_2$  and hence decreasing  $\cot\phi$ , which conveys a decrease in  $C$  while  $S_1$  is fixed. Overall, thermodynamic equilibrium is in such way reached when growing entropy encounters irreversible decreasing heat capacity at the equilibrium point. Irreversible heat capacity thus serves as an indicator for thermodynamic equilibrium. It will be disclosed in the following section that the effective factor for the existence of a maximal entropy is the lowering of internal heat.

## Irreversible heat capacity as thermodynamical analogue of Boltzmann $H$ in approaching thermodynamic equilibrium

The preceding decrease of heat capacity in approaching thermodynamic equilibrium is alike to the decrease of statistical magnitude  $H$  of Boltzmann  $H$  theorem. For the present purpose this theorem can be set forth in an elemental manner as  $dH/d\tau \leq 0$  (sign = at equilibrium),  $dS/d\tau \geq 0$ ,  $k_B H = \text{const} - S$ , with  $\text{const} = S_0 + k_B \ln P^0$  ( $P^0 = N^N$ ) [4]. In thermodynamical analogy, such constant may be set by the entropy at equilibrium,  $S_2$ , and a constant  $b$  (as if intercept  $a$  for  $T = 0$  in Figure 3), then  $\text{const} = S_2 + b$ . Using this expression for the constant of the statistical equation, it gives  $k_B H = S_2 - S + b$ . In this manner, magnitude  $H$  is connected to the increment of entropy required to reach the equilibrium.

Then using  $k_B H = S_2 - S + b$  and eq. (29) ( $S = TdS/dT$ ) and taking into account that  $dS/dT$  is constant ( $\cot\phi$ ), eq. (38) results. This equation correlates Boltzmann  $H$  with temperature ( $T_2$  equilibrium temperature).

$$H = \frac{T_2}{k_B} \left( \frac{dS}{dT} \right)_2 - \frac{T}{k_B} \frac{dS}{dT} + \frac{b}{k_B} = \frac{\cot\phi}{k_B} (T_2 - T) + \frac{b}{k_B} \quad (38)$$

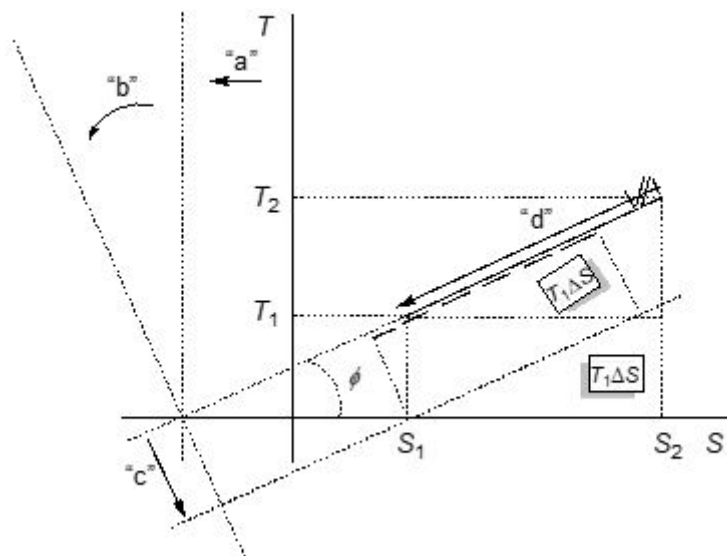
### Integration of the differential entropy-time equation. Entropy maximum

In connection with integration of eq. (21) ( $dS/S = k d\tau$ ) the low limit of entropy may be argued against as the system cannot depart from thermodynamic equilibrium but for an external influence, which is contrary to the thermodynamically isolated status of the system. However, from the thermodynamical standpoint the way whereby the system leaves equilibrium is not a point to be dealt with. It is thermodynamically sufficient and correct to take directly the low limit entropy value for an equilibrium entropy, regardlessly to whether entropy is actually thermodynamically defined or not at the starting point. Anyway, a statistical nonequilibrium analogue entropy may be used. For pseudoreversible transformations (mentioned in Introduction) that are in advance going on at the moment that would be thermodynamically isolated, their proper equilibrium entropy at that moment is to be used as the initial entropy value.

Integration of eq. (21) provides function  $S = S_1 \exp k\tau$ . This function is fitted to normal conditions by means of a counterclockwise  $180^\circ$  rotation of the coordinate axes, which gives  $S = S_2 - (S_2 - S_1) \exp -k\tau$ . In this function, final  $S_2$  is asymptotic to time. The rotation is permissible as differentiation of the transformed function restitutes eq. (21) although with the opposite sign.

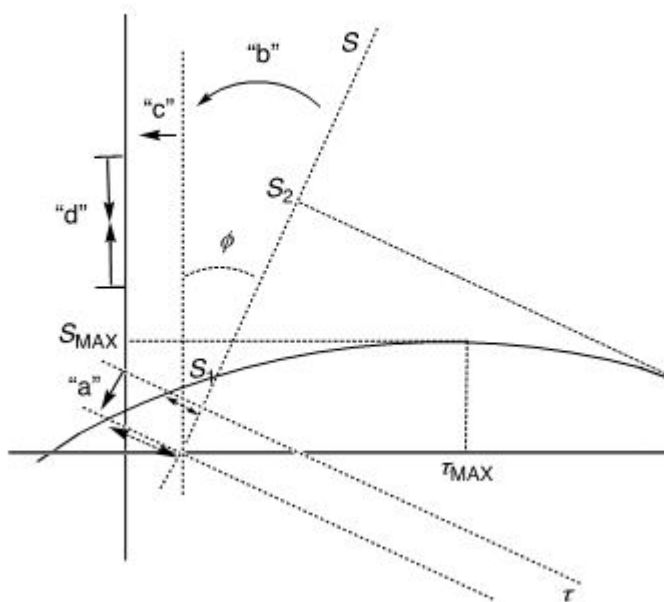
The correlation of temperature with entropy is linear according to eq. (29) ( $dT/T = dS/S$ ), as it has been indicated in the preceding section. Figure 4 shows the geometrical operations for converting reversible heat into minimal irreversible heat [internal heats ( $Q_i$ ) regarding the system]. The operations in the figure are: "a", translation of axes to the intercept of line  $T$ - $S$  at  $S$  axis; "b", rotation of axes by angle  $\phi = \arctan[(T_2 - T_1)/(S_2 - S_1)]$ ; "c", new translation of axes by length  $T_1$  so that line  $T$ - $S$  on rotated  $S$  axis is displaced from the axis in order to restore the irreversible heat; finally, "d", contraction of line  $T$ - $S$  by factor  $\cos\phi = (S_2 - S_1)/\sqrt{(S_2 - S_1)^2 + (T_2 - T_1)^2}$  so that the projection of distance  $(S_1, T_1)$ - $(S_2, T_2)$  onto the final  $S$  axis equals distance  $S_1$ - $S_2$ . Overall, the heat for the transformed  $T$ - $S$  function is in an exact manner the minimal irreversible heat for the process, the excess heat for reversibility (triangular area under  $T$ - $S$  line) having been eliminated.





**Figure 4:** Conversion of reversible heat (total area under the line) into minimal irreversible heat [ $Q_{IR} = T_1(S_2 - S_1)$ ]

The preceding stepwise transformation was applied to the entropy-time function (Figure 5, original coordinate system inclined). For step “a” the applicable transformation equation is  $S = S' + S_1 - T_1 \cot \phi$  ( $\phi$  is the same as in Figure 4). For rotation of axes (step “b”) the transformation equations are  $\tau = \tau' \cos \phi - S' \sin \phi$  and  $S = \tau' \sin \phi + S' \cos \phi$  [12] ( $\tau$  and  $S$  here stand for the preceding  $\tau'$  and  $S'$  in step “a”, and so further on for the subsequent steps). The rotation gives rise to a maximum in the entropy-time curve, which is inherent to the exponential character of the curve upon a rotation of axes.



**Figure 5:** Transformation of the entropy-time function [ $S = S_2 - (S_2 - S_1) \exp(-k\tau)$ ] for minimal irreversible heat (doubly tipped arrows relate to “c”)

For the translation in step “c” the transformation equation is  $\tau = \tau' + (1/k)\ln[T_2/(T_1 + T_2)]$  as results from temperature-time curve  $T = T_2 - (T_2 - T_1)\exp(-k\tau)$  [from  $dT/T = kd\tau$  (36)] taking into account the difference of the intercepts  $\tau_0$  ( $T = 0$ ) and  $\tau'_0$  ( $T' = 0$ ) at original and second  $\tau$  axis. This operation is the equivalent of step “c” in Figure 4 and brings the entropy-time function into agreement with minimal irreversible internal heat as it corresponds to the real thermodynamical process. Finally (“d”),  $S$  values are corrected by factor  $\cos\phi$  as in the above transformation of  $T$ - $S$  function.

The efficacy of the geometrical transformation of  $S$ - $\tau$  function to really incorporate the minimal irreversible heat requirement from  $T$ - $S$  function is revealed by the diminution of slopes taking place in the transformation of either function (see Figure 4 and 5). For  $S$ - $\tau$  function the pertinent slopes are the asymptote in untransformed function and the slope at the maximum which is less than the former minding the inversion of ordinate  $S$  axis that is abscissa axis in  $T$ - $S$  function.

The resulting implicit function for the transformed  $S$ - $\tau$  curve is eq. (39) whose parameter  $a$ ,  $b$  and  $c$  are expressed as shown in Appendix.

$$S + \left(\tau + \frac{a}{k}\right) \sin\phi \cos\phi = b \left\{ 1 - \exp\left[ S \tan\phi - \left(\tau + \frac{a}{k}\right) \cos\phi \right] \right\} \cos\phi + c \quad (39)$$

For finding the coordinates of the maximum of transformed  $S$ - $\tau$  curve, eq. (39) is differentiated for variable  $S$  with respect to  $\tau$ , and  $dS/d\tau$  is set as zero which gives the explicit  $S$ - $\tau$  function shown in Appendix. This function is substituted at primitive (39) for obtaining the  $\tau$  coordinate of the maximum from which the corresponding  $S$  coordinate follows by substitution at the derivative function ( $S_{\text{MAX}}$  and  $\tau_{\text{MAX}}$  are shown in Appendix). The second derivative of (39) at the maximum is shown in Appendix and points that is negative in agreement with a maximum. The simple exponential function ( $y = \exp x$ ) naturally renders a maximum for any rotation of coordinate axes between  $180^\circ$  and  $270^\circ$ , as this takes place in the present case.

## Discussion

With reference to Figure 3, keeping  $S_1$ ,  $S_2$  and  $T_1$  constant the irreversible heat takes away from increasing reversible heat as  $T_2$  increases. Thus the power of temperature to produce heat in an irreversible manner in the thermodynamically isolated system is less than to produce reversible heat. It is consistent with basic thermodynamical notion that temperatures must be infinitesimally close together in a reversible heat transfer. Furthermore, the power of temperature to give rise to entropy in an irreversible manner is lower than as to perfect reversible entropy.

Comparing in Figure 5 asymptotic ( $S_2, \tau = \infty$ ) in the original untransformed function with ( $S_{\text{MAX}}, \tau_{\text{MAX}}$ ) in the transformed function, there is a decrease in both coordinates upon the transformation. The enlargement of time in the reversible process is consistent with the notion of thermodynamical reversibility that requires a process to be infinitely slow.

The gap between entropy or time values upon the transformation refers to the reversible path for the process in comparison with the fully irreversible path. For a partially irreversible process the gap will be less, value  $S_{\text{MAX}}$  approaching  $S_2$ , and  $\tau_{\text{MAX}}$  approaching infinity. It correlates with angle  $\pi/2 - \phi$  about the rotation, the greater this angle the greater the irreversibility of the process. Differently, angle  $\phi$  stands for the degree of reversibility of the process.

The above transformation of the entropy-time function not only conforms the thermodynamical requirement of lessened heat concerning the irreversible thermodynamically isolated process, but is in addition consistent with minimal action [13], action  $A = W\tau \equiv W_1\tau = Q_{\text{IR}}\tau$ . Minimal action is fulfilled both by the reduced  $\tau$  heat on the irreversible transformation and by the reduction of time above shown.

## Pseudoreversible transformations

For this kind of transformations, defined in Introduction, the untransformed entropy-time function  $[S = S_2 - (S_2 - S_1)\exp(-k\tau)]$ , which straightforward results from the entropy-time differential equation, is valid since the actual path in these processes is coincident with the reversible path. According to the mathematical function, maximal entropy is achieved in these processes at infinite time. However, these processes are subject to inherent, general statistical fluctuations in the thermodynamical parameters [4,5]. Provided that entropy and time are thermodynamical parameters, the final equilibrium will be obscured in these processes by fluctuations and will be materially observed at finite and not infinite time.

## Conclusions

Internal volume is a genuine magnitude in an isochoric adiabatic system which permits to set up a correlation between volume and entropy otherwise unattainable in thermodynamics. By means of this correlation time can be introduced into thermodynamics.

Internal volume is bound to the transforming energy of the isochoric adiabatic system which internally differentiates by itself into heat and work. Entropy indicates the weariness of the energy in the transformation of the system.

The fundamental mathematical relationship connecting the magnitudes entropy and time has been found out in this work. Time is inherent to thermodynamics and is mechanically and directly transferred from thermodynamics to mechanics by means of volume, the transfer of time being otherwise done by another extensive magnitude like electric charge.

It has been proven in the work that thermodynamic nonequilibrium alone without any extraneous factor causes in a natural manner an end equilibrium at finite time with a maximal entropy.

## Conflicts of Interest

No conflict of interest was reported by the author.

## Internal Review

This research was exempt from approval by Consejo Superior de Investigaciones Científicas.

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## Appendix

$$a = \ln \frac{T_2}{T_1 + T_2}$$

$$b = S_2 - S_1$$

$$c = T_1 \sin \phi$$

$$\frac{dS}{d\tau} = 0: S = \left(\tau + \frac{a}{k}\right) \frac{\cos \phi}{\tan \phi} + \frac{1}{k \tan \phi} \ln \frac{\tan \phi}{bk}$$

$$S_{\text{MAX}} = \frac{b \left[ 1 - \ln\left(\frac{\tan\phi}{bk}\right) \right] \cos^2\phi + c \cos\phi}{k^{-1} \ln\left(\frac{\tan\phi}{bk}\right) + \cos\phi + \sin^2\phi} + \frac{1}{k \tan\phi} \ln \frac{\tan\phi}{bk}$$

$$\tau_{\text{MAX}} = \frac{b \left[ 1 - \ln\left(\frac{\tan\phi}{bk}\right) \right] \sin\phi + c \tan\phi}{k^{-1} \ln\left(\frac{\tan\phi}{bk}\right) + \cos\phi + \sin^2\phi} - \frac{a}{k}$$

$$\left( \frac{d^2S}{d\tau^2} \right)_{\tau_{\text{MAX}}} = - \frac{\left[ bk^2 \ln\left(\frac{\tan\phi}{bk}\right) \right] \cos^3\phi}{1 + \left[ bk \ln\left(\frac{\tan\phi}{bk}\right) \right] \sin\phi}$$

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