

Entropy-Time Relationship in an Isochoric Adiabatic System

Francisco Ros (✉ iqmr322@iqm.csic.es)
Instituto de Química Médica (CSIC)

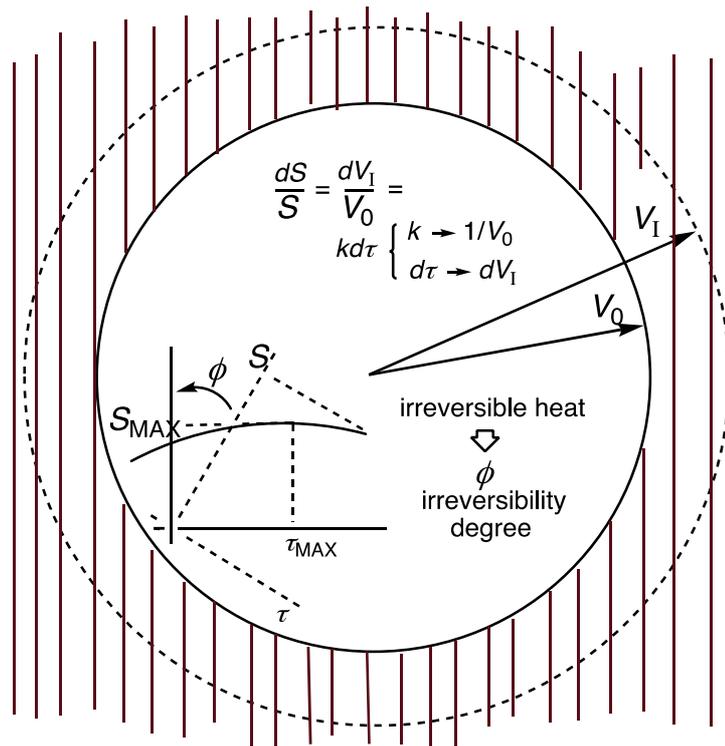
Research Article

Keywords: Irreversibility thermodynamics, Entropy-time equation, Maximal entropy, Boltzmann H, Thermophysics

Posted Date: March 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-333915/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)



Reversible process

$$S = S_2 - (S_2 - S_1)e^{-k\tau}$$

Actual irreversible process

$$S + (\tau + a/k)\sin\phi\cos\phi = b\cos\phi\{1 - e^{k[\tau\sin\phi - (\tau + a/k)\cos\phi]}\} + c$$

GRAPHICAL ABSTRACT

Entropy-Time Relationship in an Isochoric Adiabatic System

Francisco Ros*

Instituto de Química Médica, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006 Madrid, Spain; iqmr322@iqm.csic.es

ABSTRACT

The fundamental equation that connects the magnitudes entropy and time has been found out by static thermodynamics for the first time: $dS/S = dV_I/V_0 = kd\tau$, V_I internal volume. Constant k also equals $dT/Td\tau$ and is an individual characteristic for each isochoric adiabatic system in evolution. The constancy of k does not hold for a nonisochoric adiabatic system. In such manner time is introduced in the frame of thermodynamic variables as a genuine magnitude. The theoretically deduced entropy-time differential equation is empirically upheld by Newton cooling law. It was found in connection with an a priori, uncritical notion of thermodynamic equilibrium that irreversible heat capacity ($C_{IR} = T\Delta S/\Delta T$) drawing near to thermodynamic equilibrium is an indicator for the equilibrium. C_{IR} is alike to statistical Boltzmann H in the approach to thermodynamic equilibrium, and the undisclosed connection of H with

temperature is presented. The integrated entropy-time equation was modified by rotation of the coordinate axes to fulfill the necessary thermodynamic condition that pertinent irreversible heat ($Q_{\text{IR}} = T\Delta S$) is smaller than reversible heat ($dQ = TdS$), which is not embodied in the primitive S - τ differential equation. This thermodynamically indispensable rotation gives rise to an otherwise naive maximal entropy and an entropy-time maximum point. The transformation conveys a contraction of both entropy and time and is in agreement with the principle of minimal action.

Keywords: Irreversibility thermodynamics; Entropy-time equation; Maximal entropy; Boltzmann H ; Thermophysics

1. Introduction

In a previous work we used entropy in a molecular solid to determine thermodynamic quantities of state^[1]. The work proceeded with experimental thermodynamic 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 overall internal energy of the solid and 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^[2].

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

Any stage in such adiabatic processes ($Q = 0$) can be a state of "apparent" thermodynamic equilibrium if the temperature and the pressure (or generalized force Y for p) are uniform in the system at a moment in the process. Then the entropy will be a definite quantity along the process in accordance with the equation of state of the system. However, such ongoing intermediate states may not be of true equilibrium in thermodynamic sense. For instance, a thermally isolated chemical reaction that would enough slowly take place is a well-known case of a perfect succession of equilibrium states in agreement with an equation of state. 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 is unnatural and nonsensical. Actually, such a chemical reaction reaction is thermodynamically irreversible in strict sense because moves along with increasing entropy as is an adiabatic process wherein irreversibility must be adhered according to second principle. From the thermodynamic viewpoint such apparently reversible transformations may be called "pseudoreversible", and they will considered below in addition to normal irreversible processes. These often approach reversibility sufficiently well in practice^[3].

Objectives 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 searched for a general and mathematically explicit expression of such a function. The search has been undertaken for a system adiabatic as well as isochoric, *i.e.* at constant volume or, in general, not producing or receiving work ("isochoric adiabatic" same as "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 two sides of a thermodynamic equation. This brings about coefficients of flux as newly generated and sometimes awkward or meaningless quantities, or brings about artificially predetermined kinetics. Such an operation makes time be a contingent magnitude and eludes the important point. 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 magnitude time into the body of thermodynamics.

As concerns this matter of time the key equation for an adiabatic system at constant volume is differential equation (1) connecting entropy and volume. This equation has been theoretically deduced in the work, using methodology of classical thermodynamics [4,5] and rigorous, logical physico-mathematical reasoning.

$$\frac{dS}{S} = \frac{dV_1}{V_0} \quad (1)$$

The concept of *internal volume* (V_1), which is associated with the concept of *internal work*, $dW_1 = pdV_1$, was used as necessary to counteract the actual constancy of volume in the process. By the first principle 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 principle, which brings about a zero equality, cannot be used, whereas the detailed expression of the principle is $TdS - pdV = 0$ with dS actually greater than zero (by second principle) and dV equal to zero, which is a contradiction. Internal volume is therefore needed as a replacement of real volume. It 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*, $dQ_1 = TdS$ (classically named noncompensated heat by Clausius). Internal heat in turn requires an equivalent amount of internal work since internal energy is constant. Internal volume is therefore a requisite of both first and second principles in the system.

Nonconditioned 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 $dS/S = dV/V$ holds for 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 system. The correctness of the mathematical deduction leading to (1), which simultaneously refers to a constant volume and the differential volume, will be rigorously and exhaustively demonstrated below. The uniqueness of the deduction in the frame of thermodynamic variables will be analyzed. Also, the validity of modified equations to a merely adiabatic system (nonisochoric) and several other systems is pointed out.

Straightforward introduction of time into eq. (1) by the right hand side of the equation gives a first order law with respect to time for the rhythm of increase in entropy ($dS/S = kd\tau$, 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 relationship between entropy and time. Time is the only pertinent and fundamental magnitude lacking in the frame of thermodynamic 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, what warrants the soundness of the substitution. The introduction of time will be justified in details.

In order to obtain empirical support for the theoretical bringing of time, experimental Newton cooling law concerning heat flux ($dQ/d\tau$) was examined, as adapted to the system. By a dimensional analysis this law in a formal manner converts into an equal expression of the entropy-time equation resulting from eq. (1) by the introduction of time, validating this operation. As to constancy of the velocity parameter, conformity of the experimental law to the theoretical equation turns out complete when the number of variables in the system is considered.

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 integrated entropy-time function [$S = f(\tau)$]. It will be shown that irreversible heat capacity ($C_{IR} = Q_{IR}/\Delta T = T\Delta S/\Delta T$) serves as a quantitative indicator for equilibrium which complements an indefinite growth of entropy. 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 presented.

Equilibrium in natural thermodynamic systems is reached at a finite time according to empirical knowledge. By the integrated entropy-time function describing the reversible path of the process for the real irreversible path (necessarily irreversible as $\Delta S > 0$), maximal entropy was asymptotic to time. However, the primitive, unintegrated entropy-time differential equation misses the indispensable condition of minimal irreversible heat (second principle, Clausius inequality, $dQ_{IR} < TdS^{[4]}$), as such a differential equation refers to infinitesimal, reversible increments of entropy. Therefore, the integrated function was modified according to that unavoidable requirement, giving in this manner a mathematical function for the relation of entropy and time that is satisfactory as to the existence of a maximal entropy at a finite time.

The number of independent variables in the system is previously analyzed as is crucial in the deductions. Also, the pertinent assisting thermodynamic functions of variables are examined as are indispensable for the deductions, and the fundamental thermodynamic correlations for the system that thereby arise are set forth. A nomenclature for the variables 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 |
| 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 |

| | |
|--------|--|
| U | Internal energy (total energy content); Assisting internal-energy function |
| V | Volume |
| V_1 | Internal volume |
| V_0 | Volume of isochoric system |
| W | Work |
| W_1 | Internal work |
| ϕ | $\text{arccot}(dS/dT)$ (ϕ degree of irreversibility) |
| τ | Time |

Table 1. Nomenclature of variables and symbols

2. Basic equations for the reversible and irreversible processes

Since the system is adiabatic and nonworking ($Q = 0, W = 0$), the principle of equivalence $\Delta U = Q - W$ (general expression of first principle) 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 Objectives and attainments.

$$Q_1 = W_1 \quad (2)$$

As a work, internal work can be expressed by generalized force Y and generalized internal displacement X_1 for a detailed expression of first principle, eq. (3) ($p dV_1$ in particular). Quantity Y refers to an actual force in the system, in particular external mechanical pressure ($p > 0$). Although internal work may be evaluated, is not real work or effective energy. Real profitable work can be produced within the thermodynamically isolated enclosure considered. However, when the process stops by itself no effect of work remains, this useful energy being fully converted into internal heat [eq. (2)]. It is in this sense that internal work is meant.

$$T dS = Y dX_1 \quad (3)$$

The total internal heat and work for the process can be expressed as in eq. (4) where T_1 is the initial temperature and Y_1 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_1 may be an unmeasurable quantity, as V_1 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 internal heat and work in comparison with a reversible path. Figure 1 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).

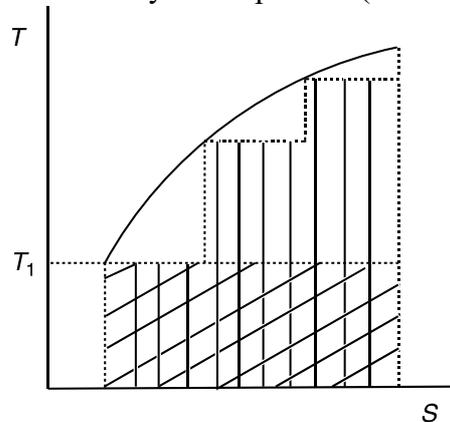


Figure 1. Irreversible heat

The reference temperature for the amount of irreversible heat is the low temperature. Thus, by second principle the heat that is transferred in an irreversible manner cannot be greater than the reversible heat, *i.e.* $dQ = TdS$, $dQ_{\text{IR}} < TdS$. This holds even though heat flux in the present system is actually toward high temperature. 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 an irreversible expansion of a substance (it is shown below that p and V_1 as well as T increase in the present transformation).

The concept of minimal irreversible internal heat, as depicted in Figure 1, is crucial for the isochoric adiabatic system as it will be shown that the maximum of the entropy-time curve rises because of this condition.

3. Variables in the thermodynamically isolated system

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 the system (*e.g.* in an electric 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 can be brought about.

The state of the thermodynamically isolated system can be thus defined with two thermodynamic variables, in the same manner that to a single substance [*e.g.* $f(U, T, Y) = 0$, internal volume plays the role of normal volume (V)], and such two variables are in turn not independent from each other since internal energy is constant. Therefore, just one variable is sufficient to specify the state of the system. 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 degrees of freedom of the system (number of independent variables) are in reality zero and not one since internal volume is not a real physical variable. Actually, $dU = TdS - pdV$, with $dU = 0$ and $dV = 0$, then here $dS = 0$. This lack of degrees of freedom is most relevant to the significance of experimental Newton cooling law for the system in evolution as it will be discussed below.

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

4. Assisting thermodynamic 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 be a constant having an arbitrary value which is set to zero for easiness [eq. (5)]. This functional expression adequately connects the variables for the system in a formal, operative manner. Enthalpy and free energy are defined by eq. (6) and (7), fittingly to eq. (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.

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

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

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

The assisting functions (5)-(7) are pertinent to a system which undergoes a change merely at constant internal energy, *i.e.* $dU = 0 = TdS - pdV$ with bulk V for V_1 . This form of the basic equation (3) is also appropriate for a thermally isolated system (an adiabatic system) producing work even though internal energy is not constant in this

case. Thus, in an irreversible, spontaneous adiabatic process entropy increases (Clausius inequality^[4]). The internal heat concomitant to the 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, and the corresponding assisting function 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 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 and internal work dW_1 according to basic eq. (3) ($TdS - pdV_1 = 0$). In term SdT , entropy may be considered a formal equivalent of heat capacity ($dQ_1 = CdT$)^[3], and internal volume in $V_1 dp$ a coefficient of pressure for work, taking $dW_1 = V_1 dp$ rather than its actual definition $dW_1 = pdV_1$. It will be disclosed below 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 and that their coefficients are functions of only one variable as pointed out in the preceding section, what allows for derivatives at (11) be total rather than partial. Eq. (3) and (8) do not give rise to a Maxwell equation such as (11) (as it is the case when dU and dG are not null) because are differentials equal to zero what instead results in a zero equality instead of an explicit equation like (11). Eq. (11) stands for the Maxwell relationship 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 mentioned in the antecedent paragraph).

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

Thermodynamic correlations

Temperature increases in the transformation considered 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 actual flux of internal heat to 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 the following section that the increase in temperature in the process 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). 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 at the expense of the internal energy reduces the temperature of the working adiabatic system. This will be further shown in the following section.

By consideration of precedent equations the following additional correlations for the isochoric adiabatic system come out. Internal volume increases in 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), and pressure increases in the transformation as temperature does. Gradient dV_1/dp is positive for the thermal evolution 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 can be extended to nonchemical systems. In reference to an electric system, charge is unloaded as entropy increases in the thermodynamically isolated system, *i.e.* $TdS = -\varepsilon dq$ [eq. (3) with the applicable sign of electric work] with $dS > 0$, hence $dq < 0$. At the same time, electromotive force decreases, *i.e.* $SdT + qd\varepsilon = 0$ [electrical analogue of eq. (8)] with $dT > 0$, hence $d\varepsilon < 0$.

5. Deduction of the 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 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, *i.e.* $dU = -dQ_1 = -TdS$, then $TdS - pdV = 0$. Accordingly, in an irreversible, spontaneous adiabatic transformation the attendant increase in entropy conveys an expansion. Otherwise, a decrease of the entropy with a contraction will occur in nonspontaneous adiabatic transformations which are not subject to second principle as they are not spontaneous. Thus 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, which may in general be variable ($dV_1/V_1 = x d\tau = dS/S$). 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, not merely a property, in the thermodynamic frame of variables. This difficulty can be overcome by means of the actual constancy of volume for the system considered, as it will be shown in the following.

5.1. Deduction with the particular assisting thermodynamic function

Putting the basic equation (3) ($TdS = pdV_1$) 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 consistent with the result obtained by differentiating the appropriate particular assisting thermodynamic 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 .

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

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

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

Eq. (17) can be obtained in an 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, the first principle (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 real internal energy as it is. This substitution of dU^* for zero permits the management of first principle for the system esteeming both the actual constancy of volume and the entropy increase. The applicable assisting thermodynamic function is in this case eq. (19), which relates to all the concerned quantities. Differentiation of this equation and subtraction of (18) gives back eq. (17).

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

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

Beyond the preceding physical interpretation and from a 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, on which we proceed in the following.

With the purpose 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 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), which is generally valid regardless of the particular V_0 value and in which dV_1 is not null. This operation results in equation $dS/S = dV_1/V_0$ [(1)], which expresses the key relation between entropy and volume for the isochoric adiabatic system.

The interpretation to key equation (1) is as follows. In auxiliary equation (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 the resulting equation (1) provides the analytical solution to the $S-V_1$ relation at the V_0 value, *i.e.* $f_0(S, V_1) = 0$ as the integral of (1).

Finally, in a dimensionally permitted manner the adimensional right hand side of eq. (1) is equated to a time differential multiplied by a frequency, which for homogeneity with $1/V_0$ is set as constant [eq. (20)]. This substitution of time gives rise to the entropy-time equation for the isochoric adiabatic system, eq. (21), by means of (1). In eq. (21), quantity k stands for a constant, independent of any variable in the system being as it is a replacement of $1/V_0$. It is characteristic to each thermodynamically isolated process and has the dimension of a first order velocity constant or of a frequency (τ^{-1}).

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

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

5.2. Discussion

5.2.1. Exclusiveness of entropy-volume equation (1) and (13)

Differential $V_1 dp$, a term of dpV_1 , can be in a correct manner taken as a substitute for work pdV_1 in the differential equations, what brings about further relations between the variables T , S , p and V_1 as well as V_0 , in addition to the relations above indicated. However, these extended relations do not include neither the key entropy-volume equation for the system [$dS/S = dV_1/V_0$ (1)] nor generic (13) ($dS/S = dV_1/V_1$), which sustain the entropy-time equation for the system.

In the manner of such an exchange and for the condition of constant volume, basic equation (3) ($TdS = pdV_1$) converts into (22). Dividing this equation by dT , eq. (23) results whereby the so-called heat of transfer Q_T stands for quantity $-T^2 dS/dT$ (multiplying both terms of the middle fraction by T). Eq. (23) regarding Q_T for a thermodynamically isolated system has been independently derived by a different method [ref. 4, p. 415] that does not involve the exchange of pdV_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.

$$TdS = V_0 dp \quad (22)$$

$$\frac{dp}{dT} = \frac{T}{V_0} \frac{dS}{dT} \equiv -\frac{Q_T}{V_0 T} \quad (23)$$

For variable volume (V_1), basic equation (3) converts into (24) by substitution of work for $V_1 dp$. This equation together with the assisting function for internal energy ($TS - pV_1 = 0$) and Maxwell equation (11)—these latter equations holding in regard to (24)—produce (25)-(27) by the usual methodology. Eq. (25)-(27) correspond to (8), (12) and (13), respectively (which arise from the regular basic equation unsubstituted for work as above described), and remarkably do not comprise the generic entropy-volume equation (13).

$$TdS = V_1 dp \quad (24)$$

$$\frac{dV_1}{dT} = \frac{S}{p} \quad (25)$$

$$\frac{dV_1}{dT} = \frac{V_1}{T} \quad (26)$$

$$\frac{dS}{S} = \frac{dp}{p} \quad (27)$$

Similarly, eq. (22) with Maxwell equation gives (28) which is analogous to particular entropy-volume eq. (1) ($dS/S = dV_1/V_0$), but refers to temperature not containing the entropy. The preceding deductions not yielding the entropy-volume relationship for the system [eq. (1) and (13)] manifest the exclusiveness of the deduction above presented in this section for the relationship.

$$\frac{dT}{T} = \frac{dV}{V_0} \quad (28)$$

5.2.2 Entropy-temperature relationship for the system

By correlations in the sets of equations departing from $TdS = pdV_1$ and $TdS = V_1 dp$, the equality of the two terms of the differential of nominal heat TS (dTS) or of work pV_1

(dpV_1) comes out. 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 points out that entropy is equal to heat capacity for the thermodynamically isolated system ($C = dQ_V/dT = TdS/dT = S$), as it has been advanced in section 4^[3]. 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.

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 of the equations for the former system are applicable to the latter system by replacing internal volume by volume and realizing that entropy relates to external heat rather than to internal heat.

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 eq. (14) ($dS/S = dV/V$, applicable to the merely adiabatic system) and negative (33), and eq. (32) similarly results from general pressure-temperature relationship (12) ($dp/p = dT/T$) and again (33). Negative (33) arises from the exchange of term Vdp by pdV concerning the merely adiabatic system, whereby the applicable basic equation and assisting function are $TdS + Vdp = 0$ and $TS + pV = 0$, while the applicable Maxwell equation is eq. (11) as usual. The change of sign in the former equations renders the correct compressibility [eq. (32)].

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

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

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

5.2.3. Nature of the introduction of time

The following arguments independently complement the introduction of time by eq. (21) ($dS/S = kd\tau$).

1. The existence of a physical relationship between entropy and time is implicit in Clausius inequality as applied to a thermally isolated irreversible transformation since the sign of the change in entropy is predetermined regarding a natural transformation which takes place in time. Such a relationship is also implied in Prigogine theorem concerning the rhythm of production of entropy. Also, time is implied in Boltzmann H theorem regarding the time for reaching equilibrium ($dH/d\tau$), statistical magnitude H being closely connected with entropy. The natural relationship of entropy and 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 the entropy-volume equation (1) ($dS/S = dV_1/V_0$). Ahead of this, a relationship of primitive character between volume and time is a logical outgoing since volume represents a length or a spacial 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 concerning 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 eq. (20) ($dV_1/V_0 = kd\tau$) is correct since represents a regular mechanical kinetics.

3. Velocity laws of zero order [like eq. (20)] actually take place in nature, *e.g.* in chemical kinetics [ref. 6, 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 inner character of internal volume.

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 frame of thermodynamic variables.

5. The replacement of internal volume by time repairs the frame of experimental thermodynamic parameters since internal volume is not a real parameter yet time is. This restitution is demanded by entropy, giving back complete the frame of paramers. Time becomes a genuine physical magnitude in the isochoric body.

6. Significance of Newton cooling law to entropy-time equation (21). 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 exterior heat ($T - T_E > 0$), whereas internal heat is produced in the thermodynamically isolated system against high temperature. As regards the thermodynamically isolated system in evolution, such a difference of temperatures is taken for a finite increment of temperature taking place 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 internal heat in the system ($dQ \equiv -dQ_1 = -TdS$). Such two considerations render eq. (34) to the system.

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

Eq. (34) in form $dS/d\tau = k_N \Delta T/T$ may be compared with the 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 is no more than a phenomenological coefficient. Thus k_N is considered dependent of one variable as it was discussed for the thermodynamically isolated system in section 3, and in particular the temperature may be considered as the variable for k_N .

The dimensions of k_N are entropy divided by time, and it can be expressed as a fraction of the actual entropy to the time multiplied by an adimensional variable, *i.e.* $k_N = xS/\tau$. Independent variable x is indispensable for a match of actual quantities. In an alternative way the relation of k_N with entropy and time can be found out recalling the coincidence of heat capacity and entropy for the system. Thus using eq. (29) ($TdS = SdT$) in (34) and 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 $\delta' = d\tau/\Delta\tau$. Setting this k_N in eq. (34) results in (35).

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

Eq. (35) is comparable with the entropy-time equation (21), to which is equivalent in meaning [$k \equiv y\Delta T/(T\Delta\tau)$]. 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 means of the unilateral manner described in the

preceding section. Nevertheless, the constancy of k as derived from Newton law remains a question.

By eq. (36) the velocity constant of the entropy-time equation is the gradient of temperature with respect to time by 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 be also obtained directly equating (21) and (28).

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

The relation of the velocity constant to Newton law constant is given by eq. (37), as it ensues equations above. This equation does not contradict the constancy of k , as factor k_N is variable (as above mentioned) likewise 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 Newton law, while it is theoretically constant.

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

For a complete match of Newton law to the entropy-time equation it is necessary to consider the actual constancy of volume for the system in adapting the law to the system. Internal volume is here not pertinent and constancy of volume is a point not embodied in Newton law. Consequently, the degrees of freedom of the system concerning variables are one less, being in reality zero as pointed out in section 3. It follows that adapted k_N as well as k in eq. (37) must unavoidably be constants, variable factor $\Delta T/TS$ here figuring a constant with regard to the isochoric system.

The constancy of k , as results from such a loss of a degree of freedom, can be further justified. Thus, differential $d\tau$ in eq. (36) is accordingly taken as a constant infinitesimal quantity (as above indicated δ') rather than it be a variable differential. As concerns dT/T in this equation, the dimensional use of Wien first law, $\lambda T = \text{const}$ (with wave-length λ in the role of condensed volume V), brings about expression $\Delta T/T \sim \Delta\lambda/\lambda_0$ making up the requirement of volume constancy (V_0). This expression indicates that dT/T in (36) figures a constant like $d\tau$ has been taken to be, and k is hence a constant.

7. Thermodynamic equilibrium in the evolving system. Thermodynamic analogue of Boltzmann H

With the purpose to obtain 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 entropy-temperature relation (28). This was also undertaken as a purely thermodynamic complement to the statistical enunciation that maximal entropy corresponds to maximal probability.

The correlation of temperature with entropy is linear as it follows the integration of eq. (28) ($dS/S = dT/T$, Figure 2). For a fully irreversible transformation and with reference to the figure, heat capacity is expressed by $C = Q_1/\Delta T = T_1(S_2 - S_1)/(T_2 - T_1)$, taking into account the minimal heat pointed out in section 2 (Figure 1). Also, it is $C = T_1 \cot\phi$, and in these terms the initial entropy is $S_1 = T_1 \cot\phi - a$, where a is the intercept of the T - S line at the S axis. Thus S_1 is less than C by quantity a , i.e. $S_1 = C - a$. In order to fulfill the equality of entropy and heat capacity at equilibrium [eq. (28)], quantity a is to vanish at the equilibrium. This can be done on Figure 2 by a translation of the axes to the intercept, 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 intercept at the origin, not altering

distance S_1S_2 but increasing T_1T_2 and hence decreasing $\cot\phi$, which conveys a decrease in C , while S_1 is now fixe. 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 a quantitative indicator for thermodynamic equilibrium, which enlightens a naive maximal entropy. It will be disclosed in the following section that the effective factor for the existance of a maximal entropy is the lowering of internal heat.

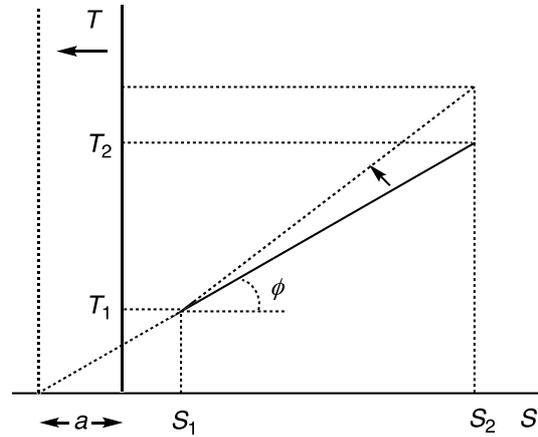


Figure 2. Change in entropy and heat capacity ($C = T_1\Delta S/\Delta T$)

The preceding set forth decrease of heat capacity in reaching thermodynamic equilibrium is theoretically alike to the decrease of statistical magnitude H of Boltzmann H theorem. This can be set forth as $dH/d\tau \leq 0$ (sign = at equilibrium), $dS/d\tau \geq 0$, $k_B H = \text{const} - S$, with $\text{const} = S_0 + k_B \ln P^\circ$ ($P^\circ = N^N$)^[4]. In thermodynamic analogy, such a constant is set by the entropy at equilibrium, S_2 , and a constant b (as if intercept a for $T = 0$ in Figure 2), then $\text{const} = S_2 + b$. Using this expression for the constant of the statistical equation 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, which is not revealed by the statistical formulation. Then using eq. (28) ($S = TdS/dT$) and taking into account that dS/dT is constant ($\cot\phi$), eq. (38) results. This equation correlates Boltzmann magnitude H with temperature (T_2 equilibrium temperature).

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

8. Integration of the entropy-time equation. Entropy maximum

With relation to integration of eq. (21) ($dS/S = kd\tau$) 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 adiabatic and isochoric status of the system. However, from the thermodynamic 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 such starting point. Anyway, a statistical nonequilibrium analogue entropy may be used. For pseudoreversible transformations (mentioned in Introduction) that are going on at the moment that are thermodynamically isolated, their proper equilibrium entropy at that moment is to be used as initial entropy.

Integration of eq. (21) provides function $S = S_1 \exp k\tau$. This function is accomodated to normal conditions by means of a counterclockwise 180° rotation of the coordinate

axes, what 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 the sign is changed.

The correlation of temperature with entropy is linear according to eq. (28), as it has been indicated in the preceding section. Figure 3 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 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 a proper manner the irreversible heat for the process, the excess heat for reversibility having been eliminated.

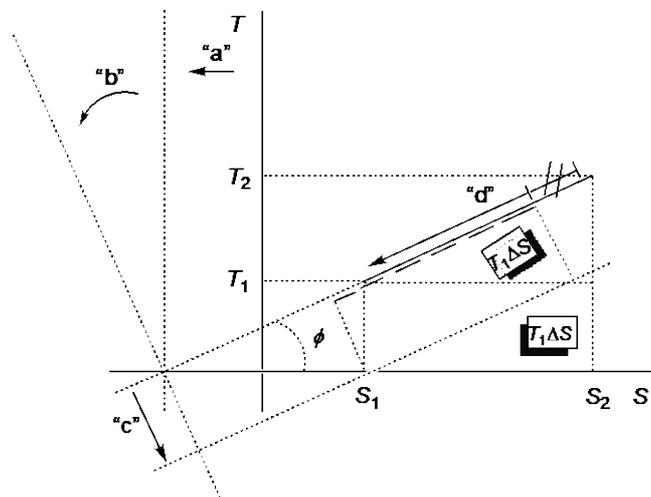


Figure 3. Conversion of reversible heat (total area under the line) into irreversible heat

The preceding stepwise transformation was applied to the entropy-time function [$S = S_2 - (S_2 - S_1)\exp(-k\tau)$, Figure 4, original coordinate system inclined]. For step "a" the applicable transformation equation is $S = S' + S_1 - T_1 \cot\phi$ (ϕ is the same as in Figure 3). For rotation of axes (step "b") the transformation equations are $\tau = \tau' \cos\phi - S' \sin\phi$ and $S = \tau' \sin\phi + S' \cos\phi$ (τ and S here stand for the preceding τ' and S' at step "a", and so further on). The rotation gives rise to a maximum in the entropy-time curve, what is inherent to the exponential character of the curve upon a rotation of axes.

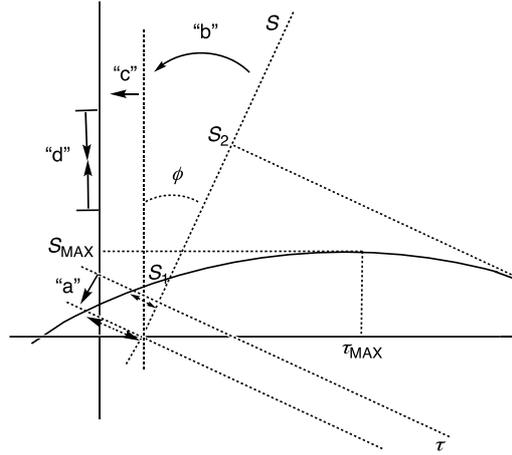


Figure 4. Transformation of the entropy-time function for irreversible heat

For the translation in step "c" the equation is $\tau = \tau' + (1/k)\ln[T_2/(T_1 + T_2)]$ as results from temperature-time curve $T = T_2 - (T_2 - T_1)\exp(-k\tau)$ [analogous to starting entropy-time curve in the figure] taking into account the difference of the intercepts τ_0 ($T = 0$) and τ'_0 ($T' = 0$) at original and second τ axis. This operation is the equivalent of step "c" in Figure 3 and brings the entropy-time equation into agreement with minimal irreversible internal heat as it corresponds to the real thermodynamic process. Finally, S values are corrected by factor $\cos\phi$ as in the above transformation of the T - S function.

The resulting implicit function for the S - τ curve is eq. (39), whose parameter a , b and c are explicited as shown in Appendix. Once the transformation is made value T_1 , T_2 , S_1 and S_2 are adjusted to real values. Angle ϕ together with k are kept as characteristics of the process.

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

For finding out the coordinates of the natural maximum of the transformed S - τ curve, eq. (39) is differentiated for variable S with respect to τ , and $dS/d\tau$ is set zero, which gives the explicit S - τ function shown in Appendix. This function is substituted at primitive (39) for obtaining the τ coordinate of the maximum, from which the corresponding S coordinate follows by substitution at the derivative function (S_{MAX} and τ_{MAX} are shown in Appendix). The value of the second derivative of (39) at the maximum is shown in Appendix and points that is negative in agreement with a maximum. The exponential function ($y = \exp x$) naturally renders a maximum for any rotation of coordinate axes between 180° and 270° , as this is at 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 internal heat in an irreversible manner is lesser than to produce reversible internal heat. It is consistent with the basic thermodynamical notion that temperatures must be infinitesimally close together in a reversible heat transfer. Similarly, the power of temperature to give rise to entropy in an irreversible manner is lower than to produce perfect reversible entropy.

Comparing in Figure 4 asymptotic ($S_2, \tau = \infty$) in the original untransformed function with (S_{MAX}, τ_{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 thermodynamic reversibility which requires a process 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_{MAX} approaching S_2 , and τ_{MAX} approaching infinity. It correlates with angle ϕ of rotation, the lesser the angle the lesser the irreversibility of the process. Angle ϕ represents the degree of irreversibility of the process.

The above transformation of the entropy-time function not only conforms the thermodynamic requirement of minimal heat regarding the irreversible thermodynamically isolated process but is in addition consistent with minimal action, action $\Delta A = W\tau \equiv W_1\tau = Q_{IR}\tau$. Minimal action is fulfilled by the reduced heat on the irreversible transformation and by the reduction of time on the other hand, either reduction as shown in the work.

Pseudoreversible Transformations

For this kind of transformations, defined in Introduction, the untransformed entropy-time function $[S = S_2 - (S_2 - S_1)\exp(-k\tau)]$ that 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 at infinite time. However, these processes are subject to inherent statistical fluctuations in the thermodynamic parameters^[4,5]. Provided that entropy and time are thermodynamic parameters on their own, the equilibrium will be obscured in these processes by fluctuations and will be materially observed at finite and not infinite time.

Conflicts of Interest

No conflict of interest was reported by the authors.

Internal Review

This research was exempt of approval by Consejo Superior de Investigaciones Cientificas.

Acknowledgments

This research was funded in part by Ministerio de Economía y Competividad grant number CTQ2010-16402.

Appendix

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

$$b = S_2 - S_1$$

$$c = T_1 \sin \phi$$

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

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

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

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

References

1. Ros F. Branched-Chain Organic Compounds. Part 11: Validation of a New Method for Determination of the Potential Energy of Cohesion of an Organic crystal and Deduction of the Heat Capacity of the Vapour. *Manatshefte für Chemie - Chemical Monthly* 2011; 142 (1): 25-37. DOI 10.1007/s00706-010-0421-2.
2. Ros F. In *Advances in Energy Research*, ed. Acosta MJ; vol. 31: 139-180. New York: Nova Science Publishers, 2019. ISBN 978-1-53616-271-4.
3. Ros F. In *Heat Capacity, Theory and Measurement*, ed. Dam SA: 1-26. New York: Nova Science Publishers, 2020. ISBN 978-1-53618-142-5.
4. Aguilar J. *Termodinámica y Mecánica Estadística* (3rd ed.). Valencia: Saber, 1969.
5. Denbigh K. *The Principles of Chemical Equilibrium* (3rd ed.). London: Cambridge University Press, 1971.
6. Benson SW. *The Foundations of Chemical Kinetics*. Malabar: Krieger, 1982. o-89874-194-7.

Figures

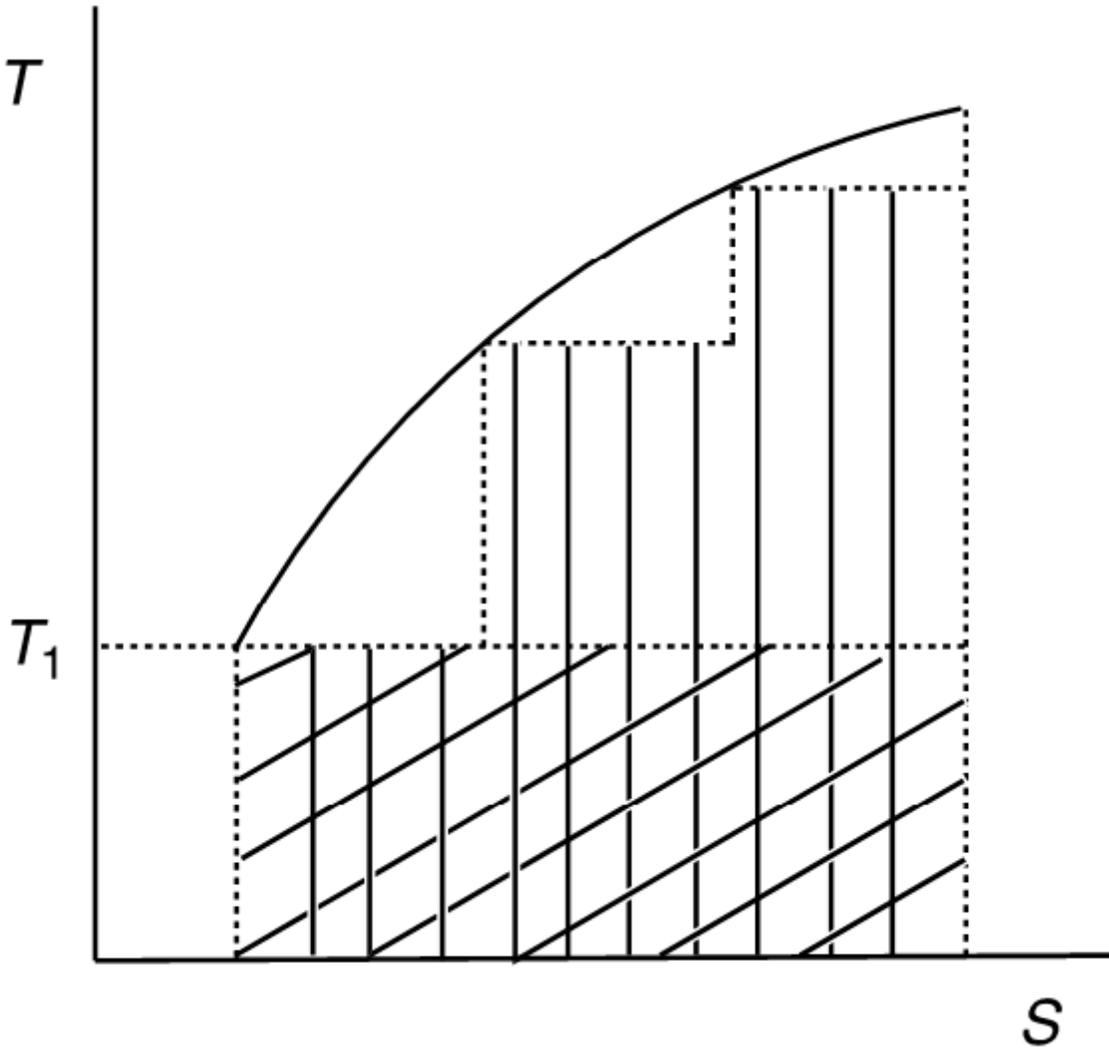


Figure 1

Irreversible heat

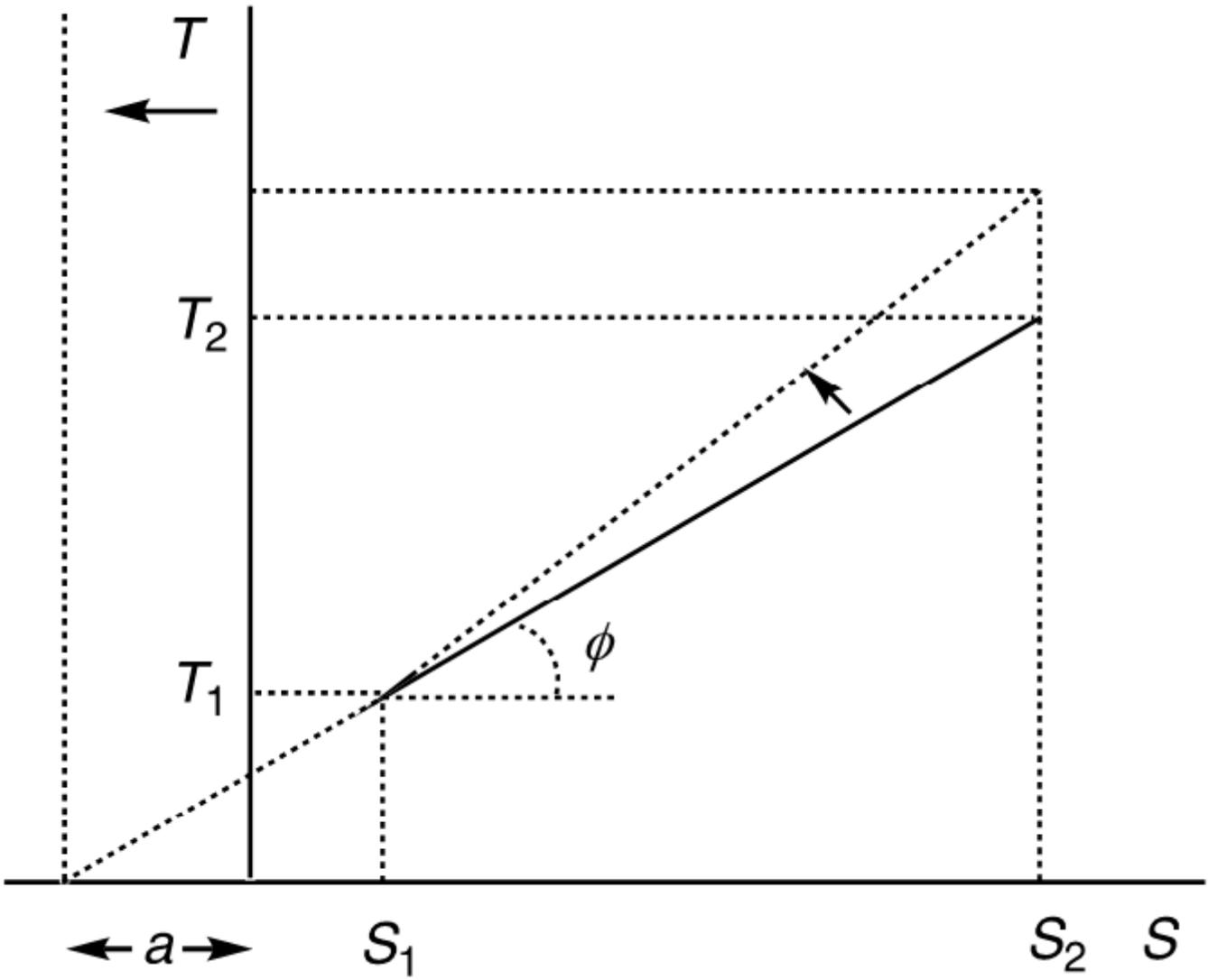


Figure 2

Change in entropy and heat capacity ($C = T_1 \Delta S / \Delta T$)

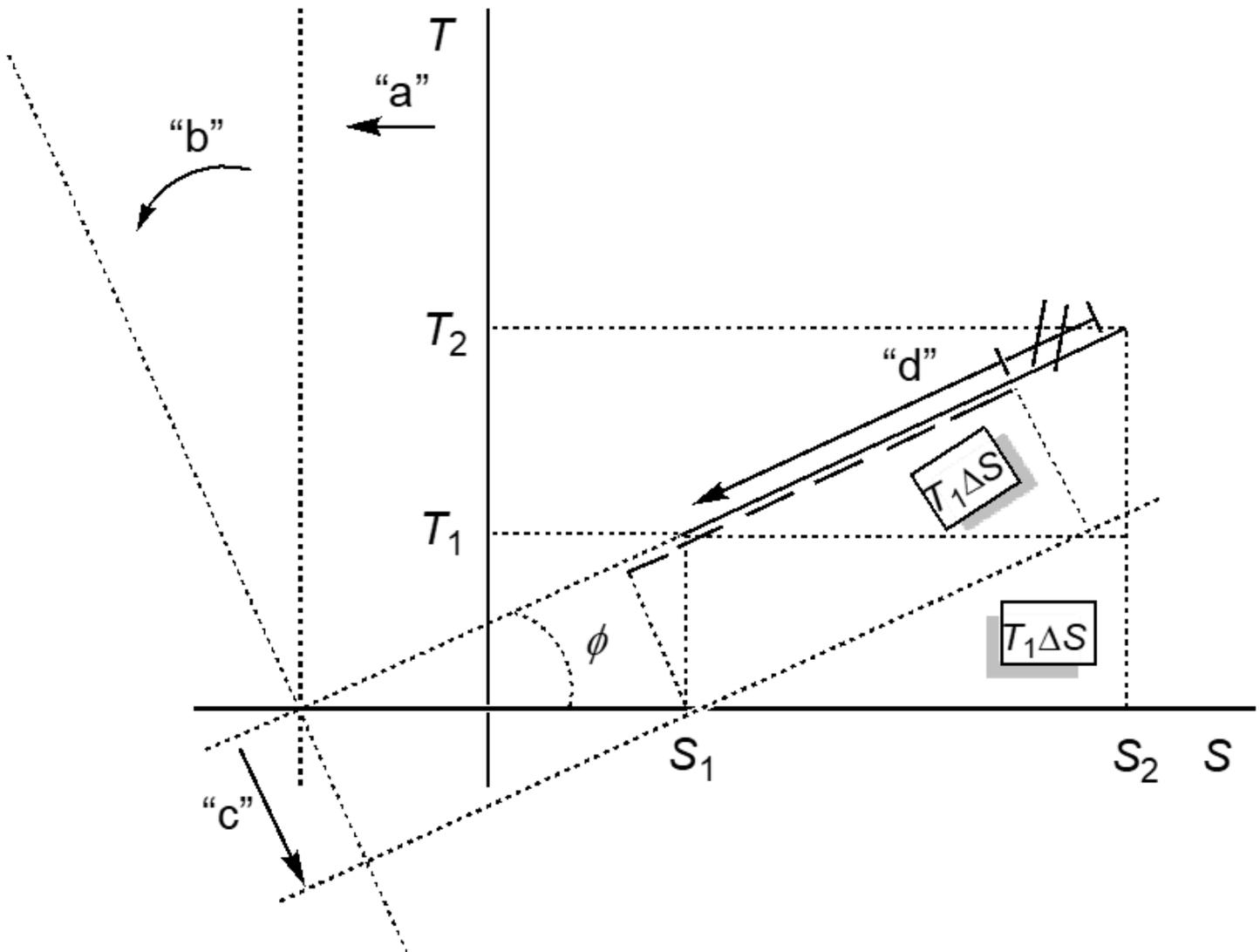


Figure 3

Conversion of reversible heat (total area under the line) into irreversible heat

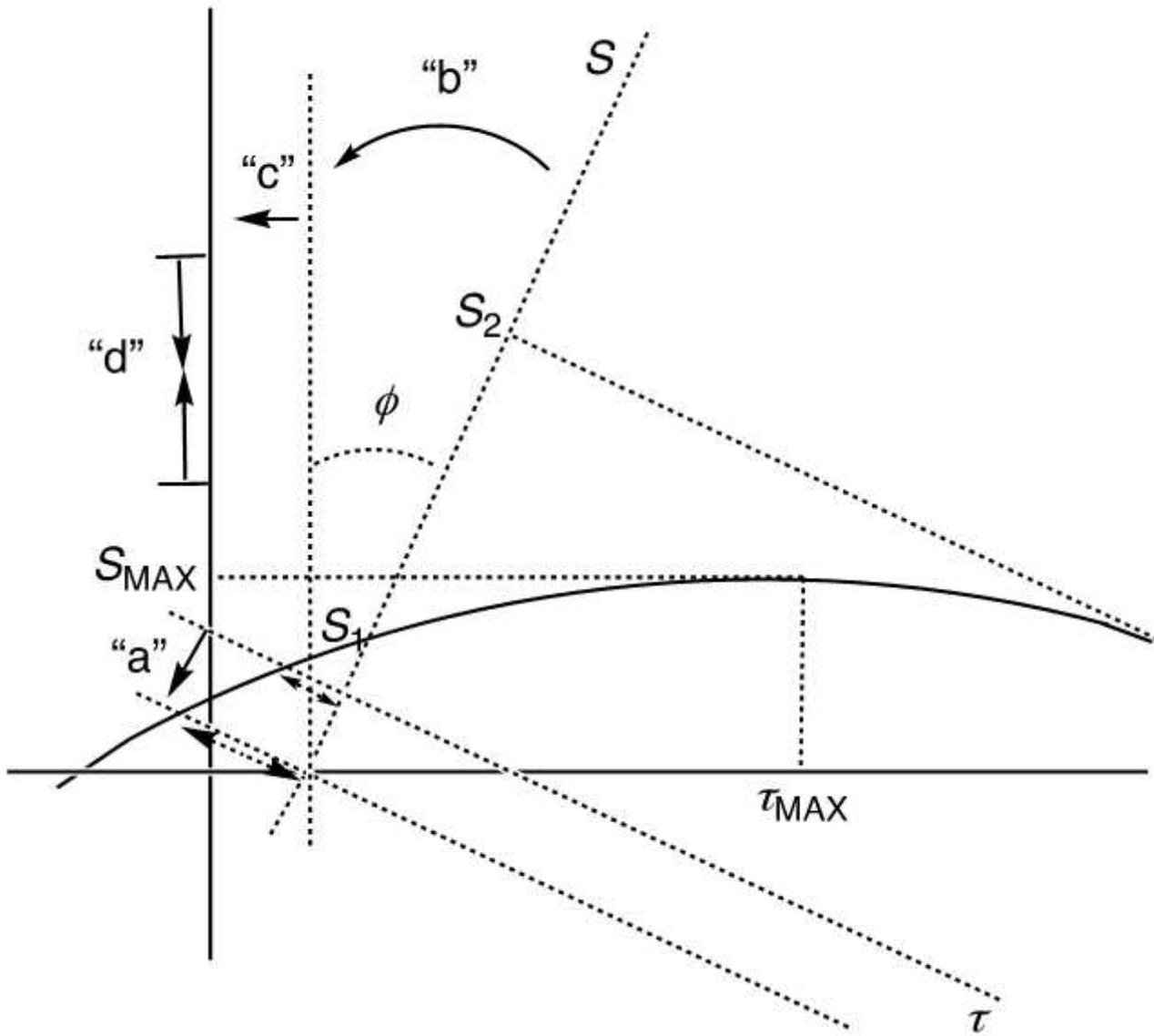


Figure 4

Transformation of the entropy-time function for irreversible heat