

# Nonextensive Approach to Thermodynamics: Analysis and Suggestions, and Application to Chemical Reactivity

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In microscopic heterogeneous reaction media, such as drops, fogs, porous substrates, micellar solutions, interpenetrated phases, chemical reactivity depends, in some cases, not only on the nature and the proportion of reactants but also on the shape, the size, and the structure of the system. This kind of behavior cannot be described in the strict framework of classical thermodynamics using extensive state functions. Physicists have shown that it is possible to extend the application field of thermodynamics to this kind of problem by using nonextensive state functions. Thus, by a statistical approach, C. Tsallis proposed a nonextensive form of the entropy which involves a fractal dimension. Although the suggested functions are interesting from a fundamental point of view, they are often difficult for the chemist to exploit. Therefore, we have attempted to tackle this problem in another way and propose a generalization of the rules of classical thermodynamics so that they can be adapted to the description of chemical reactivity in complex media. Thus, to allow the state functions to have the possibility of being or not being extensive, we propose the assumption that the state functions can be Euler's functions of the system mass with a homogeneity order,  $m$ , other than 1. For  $m = 1$ , the rules of classical thermodynamics apply. The state functions will be named "superextensive" for  $m > 1$ , and "subextensive" for  $m < 1$ . We describe the justification and consequences of these conventions and their application to chemical reactivity. The rule of additivity of the nonextensive entropy obtained by our approach is similar to that proposed by C. Tsallis.

## Introduction

Classical thermodynamics is based on using extensive state functions, that is, Euler's functions homogeneous of order 1 of the variables of extensity and in particular of the mass of the concerned system.<sup>1</sup> Applied to chemical reactivity, classical thermodynamics allows intensive extents to be defined, such as temperature, pressure, and chemical potential, independent of the system mass. Values of these variables appear directly in the evolution conditions of the system. Observation of chemical systems that are heterogeneous at the microscopic level (for example, nanosystems, porous systems, fogs, and interpenetrated media) shows that the rules of classical thermodynamics are sometimes inadequate for complete and accurate description. In some cases, chemical reactivity is not solely dependent on the nature or relative proportions of the reactants, on the pressure, or on the temperature but also dependent on the shape of the system. This topological dependence is apparent in nucleation and growth phenomena: in such cases, the chemical potentials of the compounds do not have the properties of intensive magnitudes.<sup>2</sup>

The characteristic common to all of these systems is the involvement of variables of supplementary dimension that are of lower order than the volume,  $L^3$ ; they include area,  $L^2$ ,<sup>3–6</sup> and length,  $L$ .<sup>7</sup>

The contribution of the shape of the system to its properties is not a characteristic of the system's chemistry itself. In physics, C. Tsallis<sup>8</sup> notes that, in some systems, the state variables depend

on their shape and their size: for example, the potential difference between the ends of a capacitor depends on its shape. This type of observation has lead numerous physicists<sup>9–14</sup> to consider the unicity of the thermodynamic formulations and to question the fundamental law stating that state functions must be strictly extensive. Statistical analyses different from the standard Boltzmann formalisms indicate that a different type of thermodynamics can be constructed on the basis of a nonextensive form of the entropy. Currently, the physics literature contains references to more than 20 different entropic forms.<sup>8</sup> This fruitful reflection has not been exploited or indeed even considered in chemistry. The work of Tsallis is the most illuminating of the considerations of nonextensive thermodynamics. C. Tsallis has suggested that the system entropy is linked to a fractal dimension,  $q$ , and that the entropy,  $S_q$ , of a system having a discrete number of microscopic configurations,  $W$ , can be written as

$$S_q \equiv k \frac{1 - \sum_{i=1}^W p_i^q}{q - 1} \quad (1)$$

in which  $q$  is a positive variable whose deviation from 1 measures the degree of nonextensivity of the system. When  $q > 1$ , the system is in "superextensivity". When  $q < 1$ , the system is in "subextensivity".  $k$  is a constant, the value of which generally depends on  $q$ , and it is equal to Boltzmann's constant,  $k_B$ , as  $q$  tends toward 1. When  $q = 1$ , the entropy is extensive and this expression is the same as the standard

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Boltzmann–Gibbs–Shannon formula:

$$S_1 = -k_B \sum_{i=1}^W p_i \ln p_i \quad (2)$$

The novelty of this approach concerns the nonadditivity of the entropy. Consider the entropy of a total system,  $S_{(A+B)}$ , made of two subsystems in thermal contact: A whose entropy is  $S_A$  and B whose entropy is  $S_B$ . The total entropy is equal to the sum of the entropies of each subsystem and a supplementary term describing the deviation of the extensivity.

$$\frac{S_{q(A+B)}}{k} = \frac{S_{q(A)}}{k} + \frac{S_{q(B)}}{k} + (1 - q) \frac{S_{q(A)}}{k} \frac{S_{q(B)}}{k} \quad (3)$$

The formal consequences of these definitions have been noted by C. Tsallis and by numerous other authors. Variables, including temperature and pressure, depend on  $q$  in this model and thus cease to be intensive magnitudes.<sup>8,12,13,15,16</sup>

Although this statistical approach to nonextensivity is very formally and fundamentally fruitful, its application by chemists is problematic. It is not easy for chemists to pass from formulations of entropy to significant extents, for example, affinity. We addressed the problem of the nonextensivity of state functions, not from the nonextensive entropic forms of statistical origin as proposed by physicists but through a consistent approach involving a minimum of assumptions or conventions. *The rules of classical phenomenological thermodynamics were maintained* with the aim of creating an analytical tool for chemical reactivity. Thus, we propose *another thermodynamic way to describe the behavior of systems*, including applications of classical thermodynamics within its limits. We compare the consequences of this approach to that proposed by C. Tsallis and consider points of convergence and divergence. Obviously, the objective of this study was to apply this approach to chemical reactivity, to interpret observed behavior, and, as much as possible, to predict behavior.

**(I) Extensivity and Nonextensivity of State Functions.** A clear definition of the extensivity and of the nonextensivity of the state functions is necessary for this analysis. Consider the behavior of a system made of  $n_1$  moles of compound 1 and  $n_2$  moles of compound 2. To characterize this system, there is a variable of dimension 3, volume,  $L^3$ , and another variable of a dimension  $<3$ ,  $L^p$ , named  $\chi$ , which could be an area,  $A$  ( $p = 2$ ), or a length,  $L$  ( $p = 1$ ). The introduction of this variable can be justified from observation of the studied system, because surfaces (those of liquid drops in a fog, for example) or lines (three-phase line for a sessile drop, for instance) are clearly involved in the evolution conditions of the system. This is the case for adsorption, wetting, or nucleation phenomena. The need of this supplementary variable of dimension can be also justified when the results of an a posteriori analysis of the behavior of a system reveal that the introduction of a variable of dimension 3 (volume) is insufficient to describe its behavior. This is the case of certain complex systems as dispersed media (including micellar solutions and microemulsions). By convention, a tension extent,  $\tau$ , will be associated with the variable  $\chi$  such that the product  $\tau d\chi$  accurately corresponds to an *elementary work*,  $\delta W = \tau d\chi$ . The corresponding energy is  $E_d = \tau\chi$ . Under this condition,  $\delta W$  can be introduced into an expression of the internal energy in accordance with the Cathéodory approach.<sup>17,18</sup> To illustrate the general formulas below, we will consider the particular case where  $\chi$  is identified with the area,  $A$ , and  $\tau$  with the surface tension,  $\gamma$ .

**(I.1) Definitions and Conventions.** In the conditions defined above, the variation of internal energy accompanying a reversible transformation is simply written as

$$dU = T dS - P dV + \mu_1 dn_1 + \mu_2 dn_2 + \tau d\chi \quad (4)$$

where  $U$  is a function with an exact differential toward the extensity variables.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2,\chi} dS - \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2,\chi} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2,\chi} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1,\chi} dn_2 + \left(\frac{\partial U}{\partial \chi}\right)_{S,V,n_1,n_2} d\chi \quad (5)$$

In classical thermodynamics,  $U$  is a Euler's function of order 1 with respect to its extensities ( $S$ ,  $V$ ,  $n_1$ ,  $n_2$ , and  $\chi$ ). This means that the following property must be confirmed:

$$U_\beta = U(\beta S, \beta V, \beta n_1, \beta n_2, \beta \chi) = \beta U(S, V, n_1, n_2, \chi) \quad (6)$$

To give a sense to these definitions, it is important to consider the way that the values of variables of dimension  $V$  and  $\chi$  should be modified in reversible operation, especially in the case of condensed phases (liquid and solid). Indeed, for condensed phases, the values of variables of dimension are often linked to the mass of the system. Thus, for a condensed phase, the volume itself is a Euler function of order 1 with respect to the system mass

$$V_\beta = V(\beta n_1, \beta n_2) = \beta V(n_1, n_2) \quad (7)$$

The multiplication of the mass by a number,  $\beta$ , leads to multiplying the volume also by  $\beta$ .

By adopting the definitions given by I. Prigogine and R. Defay,<sup>1</sup> *an extent is considered as extensive if it is a homogeneous function of order 1 of the mass*.

Therefore, the internal energy will be an extensive function only if each of the variables of extensity is also extensive. Thus, for the variable  $\chi$ , this leads to

$$\chi_\beta = \chi(\beta n_1, \beta n_2) = \beta \chi(n_1, n_2) \quad (8)$$

In such a case, as for the volume, when the system mass is multiplied by  $\beta$ , the value of  $\chi$  is also multiplied by  $\beta$ .

In the classical thermodynamics framework, the entropy is set as an extensive function. The internal energy,  $U$ , is then an extensive state function and has all the properties of homogeneous functions of order 1 with respect to the extensities. One can write the two supplementary equations concerning the integral form

$$U = TS - PV + \mu_1 n_1 + \mu_2 n_2 + \tau \chi \quad (9)$$

and the Gibbs–Duhem relationship

$$0 = S dT - V dP + n_1 d\mu_1 + n_2 d\mu_2 + \chi d\tau \quad (10)$$

In such cases, the variables  $T$ ,  $P$ ,  $\mu_1$ ,  $\mu_2$ , and  $\tau$ , which are derivatives of an extensive function,  $U$ , from the extensive variables  $S$ ,  $V$ ,  $n_1$ ,  $n_2$ , and  $\chi$ , respectively, are intensive extents, independent of the mass of the system.

However, in some situations, the extensivity of the dimension  $\chi$  is not confirmed. For example, the area of a spherical drop of liquid increases with its mass but the relationship is not linear. If the mass of the spherical system is multiplied by  $\beta$  ( $\beta n_1, \beta n_2$ ), at constant system composition, the volume is multiplied by  $\beta$

and the area by  $\beta^{2/3}$ . The volume obviously remains as an extensive function. However, the area is a homogeneous function of order  $2/3$  of the mass, which has the properties of Euler's functions but is not an extensive extent. Thus, *a variable of dimension  $\chi$  can vary, but not necessarily proportionally, with the system mass;  $\chi$  is therefore not an extensive variable.* This issue has rarely been considered in chemistry.<sup>19–22</sup> The introduction of a nonextensive variable in state functions violates the rules of classical thermodynamics and implies *an alternative approach of thermodynamics*: it would be important to establish the consistency of any such approach and to demonstrate the value of its application to reactivity. This difficulty can be underscored by considering the particular case in which the variable  $\chi$  depends on the system mass but is not an extensive extent:

$$\chi = \chi(n_1, n_2) \quad \text{and} \quad \chi_\beta = \chi(\beta n_1, \beta n_2) \neq \beta \chi(n_1, n_2) \quad (11)$$

If  $\chi$  is not extensive, the multiplication of the numbers of moles,  $n_1$  and  $n_2$ , by a number,  $\beta$ , will not lead to multiplying  $U$  by  $\beta$ , and consequently,

$$U_\beta = U(\beta n_1, \beta n_2, \chi_\beta) \neq \beta U(n_1, n_2, \chi) \quad (12)$$

The internal energy is not extensive and therefore is not a homogeneous function of order 1 of its extensities: when the mass is multiplied by  $\beta$ , the extensities are not.

The result is that the integral of  $U$  and the Gibbs–Duhem relationship cannot apply. This point is very important because the creation of state functions by means of Legendre transforms is not possible in this situation. Consequently, the meaning of the tension variables associated with the extensities, particularly the temperature and the pressure, causes a problem. When  $\chi$  is not extensive, temperatures  $T_\beta$  and  $T$  of systems containing  $\beta n_1$  and  $\beta n_2$  moles and  $n_1$  and  $n_2$  moles are not necessarily identical

$$T = \left( \frac{\partial U}{\partial S} \right)_{V, n_1, n_2, \chi}; \quad T_\beta = \left( \frac{\partial U_\beta}{\partial S_\beta} \right)_{\beta V, \beta n_1, \beta n_2, \chi_\beta}$$

with

$$V_\beta = \beta V; \quad \chi_\beta \neq \beta \chi \quad (13)$$

If the internal energy is not extensive, nothing indicates that the derivatives of the internal energy with the entropy are independent of the system mass (intensive magnitudes). The temperature is no longer intensive. The same reasoning should be applied to pressure and chemical potential.

In these conditions, there may be *other thermodynamic approaches using nonextensive state functions including classical thermodynamics in their limit conditions, and which allow appropriate description of the chemical reactivity of complex systems.*

The mathematical properties of fundamental relations of thermodynamics, particularly cross-differentiation properties, can be used to generate an elegant solution to this problem by formally separating extensive and nonextensive contributions to state functions.

**(I.2) Extensive and Nonextensive Contents of Variables of Dimension.** Consider a reversible transformation for which variations of the internal energy can be expressed by eq 4. Suppose that  $U$  has an exact differential toward its extensities and that the volume is an extensive extent. Suppose that the variable  $\chi$  is not necessarily extensive. Setting this condition

oversteps the framework of classical thermodynamics. Examine a general case in which the internal energy can be nonextensive, such that it is not a homogeneous function of order 1 with respect to its extensities. In these conditions, the integral equation of  $U$  and, obviously, the Gibbs–Duhem relationship cannot apply. However, with the internal energy being a state function having an exact differential, the mathematical properties of cross-differentiations can be used. For example, this following relation must be verified:

$$\left( \frac{\partial \tau}{\partial \mu_2} \right)_{S, V, n_1, \chi} = - \left( \frac{\partial n_2}{\partial \chi} \right)_{S, V, \mu_2, n_1} \quad (14)$$

In the left-hand term, variations of the tension,  $\tau$ , with the chemical potential of 2 is envisaged at constant entropy, volume,  $n_1$ , and  $\chi$ . A particular case is to suppose that this term is null. This solution cancels the problem that we are trying to resolve. The general case is where  $\tau$  varies with the chemical potential of 2 in the system, implying that the term on the right-hand side is not null. The result is that modification of the variable  $\chi$  at constant entropy, volume, chemical potential of 2, and solvent quantity ( $n_1$ ) can only occur if there is a change of the quantity of 2 in the system. This is only possible if a content corresponding to a certain number of moles of 2 is associated to  $\chi$ .

*This reasoning, which should be the same for all other variables of dimension introduced into the expression of internal energy, involves that content is systematically associated, formally at least, with the variable of dimension. Thus, content is associated with both extensive and nonextensive variables.*

Formally, this separation of contents is related to that suggested by R. Defay concerning interfacial properties. He differentiated the “unlimited phases” from the “limited phases” in which the area variable intervenes directly.<sup>3</sup> Thus, the unlimited phases are extensive, whereas the limited phases can be nonextensive. The variable of dimension  $\chi$ , which we will consider to be nonextensive, is associated with  ${}^D n_1$  moles of 1 and  ${}^D n_2$  moles of 2. The other numbers of moles in the system will be conventionally denoted by  ${}^E n_1$  and  ${}^E n_2$ . The numbers of moles of solvent 1 and solute 2 will be divided between the two contents, such that

$$n_1 = {}^D n_1 + {}^E n_1 \quad (15)$$

$$n_2 = {}^D n_2 + {}^E n_2 \quad (15')$$

Internal energy will be divided into two components: the first includes all the extensive terms, and the other includes all terms which characterize the dimension contents. Thus,

$$dU = d^E U + d^D U \quad (16)$$

Then, characteristics of these two contributions can be clarified.

For the extensive part of the internal energy,  $d^E U$ , this magnitude takes into account only the extensive variables. Obviously, the variable  $\chi$  does not appear in this expression

$$d^E U = T d^E S - P d^E V + {}^E \mu_1 d^E n_1 + {}^E \mu_2 d^E n_2 \quad (17)$$

${}^E S$  and  ${}^E V$  are extensive variables of  ${}^E n_1$  and  ${}^E n_2$ .

In these conditions, the temperature,  $T$ , and the pressure,  $P$ , are intensive extents, as are the chemical potentials of 1 and of 2 ( ${}^E \mu_1$  and  ${}^E \mu_2$ , respectively). The chemical potentials of 1 and of 2 are those defined from  $U$ , in a transformation at constant  $\chi$ . In this case, only the variable  $\chi$ , depending on  ${}^D n_1$  and  ${}^D n_2$ ,

needs to be considered. Only the variations of the extensive part of the internal energy are observed:

$$\mu_1 = \left( \frac{\partial U}{\partial n_1} \right)_{S,V,n_2,\chi} = \left( \frac{\partial {}^E U}{\partial n_1} \right)_{S,V,n_2,\chi} = \left( \frac{\partial {}^E U}{\partial n_1} \right)_{E_S, E_V, E_{n_2}} = {}^E \mu_1 \quad (18)$$

It is interesting to note the particular contribution of the volume in this approach. It is an extensive extent, and it takes into account all the moles of 1 and of 2, associated with extensive or dimension contents

$${}^E V = {}^E V({}^E n_1, {}^E n_2) \quad \text{and} \quad {}^E V_\beta = \beta^E V({}^E n_1, {}^E n_2) \quad (19)$$

$${}^D V = {}^D V({}^D n_1, {}^D n_2) \quad \text{and} \quad {}^D V_\beta = \beta^D V({}^D n_1, {}^D n_2) \quad (19')$$

Partial molar volumes of 1 and 2 are independent of the considered content. Thus,

$$V'_1 = \left( \frac{\partial {}^E V}{\partial n_1} \right)_{E_{n_2}} = \left( \frac{\partial {}^D V}{\partial n_1} \right)_{D_{n_2}} = \left( \frac{\partial V}{\partial n_1} \right)_{n_2} \quad (20)$$

$$V'_2 = \left( \frac{\partial {}^E V}{\partial n_2} \right)_{E_{n_1}} = \left( \frac{\partial {}^D V}{\partial n_2} \right)_{D_{n_1}} = \left( \frac{\partial V}{\partial n_2} \right)_{n_1} \quad (20')$$

For the nonextensive part of the internal energy, for the general case, variations will be as follows:

$$d^D U = {}^D T d^D S - {}^D P d^D V + {}^D \mu_1 d^D n_1 + {}^D \mu_2 d^D n_2 + \tau d\chi \quad (21)$$

We do not use the exponent D for the tension,  $\tau$ , because it is necessarily linked to the nonextensive term  $\chi$ . The properties of these two contributions to the internal energy should be considered.

The reasoning cannot be continued without specifying how the variable  $\chi$  is nonextensive. This requires the introduction of conventions or new properties not included in classical thermodynamics, which does not cover this kind of situation.

One possible approach would be to use that of C. Tsallis and to try to draw inferences about chemical reactivity. Thus, the relation which expresses the nonadditivity of the nonextensive entropy would, with our formalism, lead to

$${}^D S_{(A+B)} = {}^D S_A + {}^D S_B + \frac{(1-q)}{k} {}^D S_A {}^D S_B \quad (22)$$

The problem is that this last relation or the definition of the nonextensive entropy does not lead in a simple and unique way to an expression of the chemical affinity, which is our final objective. We therefore explored the classical thermodynamics, without using the statistical approach, by introducing rules of power to express the nonextensivity and thereby maintain the spirit of Tsallis' proposition.

**(II) Nonextensive Functions of State, Propositions, and Properties. (II.1) How Should Nonextensivity be Characterized?** The nonextensivity of the functions of state is caused by the introduction of variables, which are presumed to change continuously with respect to their content but are not homogeneous functions of order 1 of their dimension content.

$$\chi = \chi({}^D n_1, {}^D n_2) \quad \text{and} \quad \chi_\beta = \chi(\beta^D n_1, \beta^D n_2) \neq \beta \chi({}^D n_1, {}^D n_2) \quad (23)$$

The variations of these nonextensive variables can be very diverse according to changes in the shape, size, and structure of the system during the transformation considered.

However, the tension,  $\tau$ , must be intensive and must not vary with its content if it is an extent characteristic of the system associated with the variable  $\chi$ . If this were not the case, the surface tension of a liquid, for example, could not be defined in a single way.

Thus, this property (intensity of  $\tau$ ) can be obtained formally by assuming that the nonextensive internal energy and  $\chi$  are two homogeneous functions of the system mass of the same order of homogeneity,  $m$ , of the dimension content. This does not require that  $m$  is equal to 1.

For the variable  $\chi$ , the properties will be as follows:

$$\chi = \chi({}^D n_1, {}^D n_2) \quad \text{and} \quad \chi_\beta = \chi(\beta^D n_1, \beta^D n_2) = \beta^m \chi({}^D n_1, {}^D n_2) \quad (24)$$

$$d\chi = \left( \frac{\partial \chi}{\partial {}^D n_1} \right)_{D_{n_2}} d^D n_1 + \left( \frac{\partial \chi}{\partial {}^D n_2} \right)_{D_{n_1}} d^D n_2 = \chi'_{D_{n_1}} d^D n_1 + \chi'_{D_{n_2}} d^D n_2 \quad (25)$$

and

$$m\chi = \chi'_{D_{n_1}} {}^D n_1 + \chi'_{D_{n_2}} {}^D n_2 \quad (26)$$

with by coherence

$$(m-1)d\chi = {}^D n_1 d\chi'_{D_{n_1}} + {}^D n_2 d\chi'_{D_{n_2}} \quad (27)$$

This convention, if accepted, introduces a rule of power for the state variables and dictates that the nonextensive internal energy can be defined as a Euler function of order  $m$  of the dimension content of the system

$$d^D U = {}^D U'_{D_{n_1}} d^D n_1 + {}^D U'_{D_{n_2}} d^D n_2 \quad (28)$$

$$m^D U = {}^D U'_{D_{n_1}} {}^D n_1 + {}^D U'_{D_{n_2}} {}^D n_2 \quad (29)$$

with by coherence

$$(m-1)d^D U = {}^D n_1 d^D U'_{D_{n_1}} + {}^D n_2 d^D U'_{D_{n_2}} \quad (30)$$

Thus,  $\tau$  is an intensive extent because it comes from the derivation of a Euler's function by another function of the same degree of homogeneity.

$$\tau = \left( \frac{\partial {}^D U}{\partial \chi} \right)_{D_S, D_V, D_{n_1}, D_{n_2}} \quad (31)$$

If this extension of thermodynamics rules is accepted, then all the other magnitudes of the system are perfectly defined.

**(II.2) Consequences of this Novel Definition of Nonextensive State Functions. (II.2.1) Temperature and Entropy.** One can follow the process step by step to determine the properties of other variables.

Concerning temperature, in the developments of Tsallis' relationships, it is possible to define formally "physical temperatures" independently of "thermodynamic temperatures" for the same system at equilibrium.<sup>12,15,16</sup> Our formalism should allow this kind of result. Nevertheless, it is important for chemists that the temperature is an intensive "physical" extent identical to a thermal reservoir with which the system



is in contact. Then, it is logical to attribute to  ${}^D U$  and  ${}^D S$  the property of being homogeneous functions of the same order  $m$  of the dimension content. This is to attribute to nonextensive entropy the property of being a Euler's function with its dimension content having the same degree of homogeneity as  $\chi$ .

Under these conditions, temperature is an intensive magnitude, independent of the system mass and of its extensive and dimension contents, identical to a thermal reservoir in contact with the system

$$T = \left( \frac{\partial {}^E U}{\partial {}^E S} \right)_{E_V, E_{n_1}, E_{n_2}} = \left( \frac{\partial {}^D U}{\partial {}^D S} \right)_{D_V, D_{n_1}, D_{n_2}, \chi} = {}^D T \quad (32)$$

The inverse of the physical temperature of the system thus becomes the "Lagrange multiplier" for the extensive and dimension contents. Therefore, nonextensive entropy,  ${}^D S$ , has identical properties to those attributed by convention to  $\chi$  and  ${}^D U$ , namely,

$${}^D S = {}^D S({}^D n_1, {}^D n_2) \quad \text{and} \quad {}^D S_\beta = {}^D S(\beta {}^D n_1, \beta {}^D n_2) = \beta^m {}^D S({}^D n_1, {}^D n_2) \quad (33)$$

$$d {}^D S = {}^D S'_{D_{n_1}} d {}^D n_1 + {}^D S'_{D_{n_2}} d {}^D n_2 \quad (34)$$

and

$$m {}^D S = {}^D S'_{D_{n_1}} {}^D n_1 + {}^D S'_{D_{n_2}} {}^D n_2 \quad (35)$$

with by coherence

$$(m-1) d {}^D S = {}^D n_1 d {}^D S'_{D_{n_1}} + {}^D n_2 d {}^D S'_{D_{n_2}} \quad (36)$$

S. Abe et al. proposed a physical temperature different from the inverse of the Lagrange multiplier; they associated a nonextensive entropy to an extensive internal energy, introducing this condition as the thermal equilibrium condition of the system.<sup>12</sup> This approach and its consequences have been discussed by R. Toral.<sup>16</sup>

The proposed extension of thermodynamics rules in our approach obviously modifies the property of additivity of state functions, which is a fundamental property of classical thermodynamics.

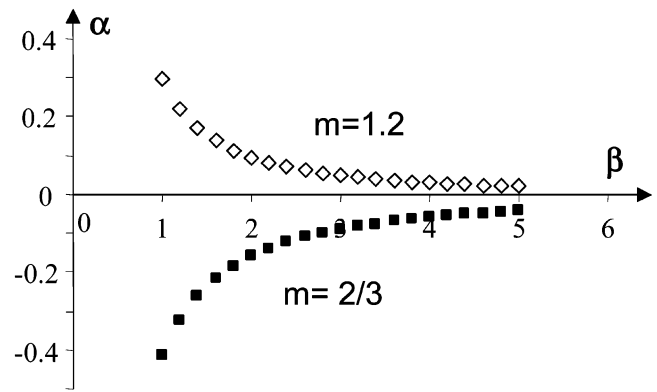
(II.2.2) *Nonadditivity of Nonextensive Functions of State.* The reasoning used hereafter for the function  $S$  is also valid for the variable  $\chi$  and the internal energy. Consider two systems: system A containing  $n_1$  moles of 1 and  $n_2$  moles of 2 and system B containing  $\beta n_1$  moles of 1 and  $\beta n_2$  moles of 2. The entropies of these two systems are

$$S_A = S(n_1, n_2) = {}^E S({}^E n_1, {}^E n_2) + {}^D S({}^D n_1, {}^D n_2) \quad (37)$$

$$S_B = S(\beta n_1, \beta n_2) = {}^E S(\beta {}^E n_1, \beta {}^E n_2) + {}^D S(\beta {}^D n_1, \beta {}^D n_2) \quad (38)$$

$$S_B = \beta {}^E S({}^E n_1, {}^E n_2) + \beta^m {}^D S({}^D n_1, {}^D n_2) \quad (38')$$

These two systems of the same composition but different masses are mixed at constant temperature. The reason these systems are not extensive is preserved, even after mixing ( $m = \text{constant}$ ). The final system has  $(\beta + 1)n_1$  moles of 1 and  $(\beta + 1)n_2$  moles of 2, which are made up of both extensive and dimension



**Figure 1.** Variations of the parameter  $\alpha$  of eq 43 with  $\beta$  for two values of  $m$ .

contents. The entropy of the system is  $S_{(A+B)}$

$$S_{(A+B)} = S((\beta + 1)n_1, (\beta + 1)n_2) \quad (39)$$

$$S_{(A+B)} = {}^E S((\beta + 1){}^E n_1, (\beta + 1){}^E n_2) + {}^D S((\beta + 1){}^D n_1, (\beta + 1){}^D n_2) \quad (39')$$

$$S_{(A+B)} = (\beta + 1){}^E S({}^E n_1, {}^E n_2) + (\beta + 1)^m {}^D S({}^D n_1, {}^D n_2) \quad (39'')$$

The deviation from additivity of the entropy is characterized by the quantity

$$\Delta_{\text{dev}} S = S_{(A+B)} - S_A - S_B \quad (40)$$

When these extents are expressed in extensive and nonextensive terms, the extensive terms are canceled, so

$$(\beta + 1){}^E S({}^E n_1, {}^E n_2) = \beta {}^E S({}^E n_1, {}^E n_2) + {}^E S({}^E n_1, {}^E n_2) \quad (41)$$

and the deviation from additivity can be characterized as the time of the mixing of the two systems by

$$\Delta_{\text{dev}} S = {}^D S_{(A+B)} - {}^D S_A - {}^D S_B = {}^D S_A [(\beta + 1)^m - \beta^m - 1] \quad (42)$$

or

$$\Delta_{\text{dev}} S = \frac{[(\beta + 1)^m - \beta^m - 1]}{\beta^{m+1}} {}^D S_A {}^D S_B = \alpha {}^D S_A {}^D S_B \quad (43)$$

For the entropy, the deviation from additivity reveals the product of nonextensive entropies of the two separate systems. The parameter  $m$  corresponds to the deviation from additivity of the system. For  $m = 1$ ,  $\Delta_{\text{dev}} S = 0$ ,  $S$  is then an extensive function.

This result reveals an interesting property of additivity. For a given value of  $m$ , that is, a fixed deviation from additivity, a form of additivity for the entropy can be found because the mass of one of the two systems is greater than the other one. As an illustration, the evolution of the parameter  $\alpha$ , when  $\beta$  varies, is given in Figure 1 for two values of  $m$ ; one value is  $2/3$ , which is found for spherical systems, and the other value of  $m$  is 1.2, which is found for the behavior of aqueous solutions containing concentrated surfactants.<sup>21,22</sup>

Values of  $\alpha$  tend toward zero when the mass of one system is greater than that of the other. Although the mixed systems are not extensive, there is additivity of the entropy. The change in  $\alpha$  has positive values for  $m > 1$  and negative values for  $m < 1$  as the value of  $\beta$  increases. The behavior thus differs, as in

Tsallis' approach, between superextensive systems ( $m > 1$ ), for which the variations of  ${}^D S$  are greater than those of the mass, and subextensive systems ( $m < 1$ ), for which the variations of  ${}^D S$  are smaller than those of the mass.

The introduction of a power law into the state functions leads to an expression which can be compared in its form to that proposed by C. Tsallis. Indeed, if the two approaches are identified, one obtains

$$\frac{[(\beta + 1)^m - \beta^m - 1]}{\beta^{m+1}} = \frac{1 - q}{R'} \quad (44)$$

so

$$q = 1 - R' \frac{[(\beta + 1)^m - \beta^m - 1]}{\beta^{m+1}} \quad (45)$$

$R'$ , which is equal to the product of the constant  $k$  (in the work of Tsallis) multiplied by Avogadro's number, is an extent which is the same as the gas constant as  $q$  tends toward 1. The relation between  $q$  and  $m$  is difficult to assess because it is not known how  $R'$  varies with  $q$ . However, it appears that these two magnitudes characterize the extensivity for  $m = 1$ , and for  $m < 1$ ,  $q > 1$  (subextensivity), and for  $m > 1$ ,  $q < 1$  (superextensivity).

Thus, we show using very different approaches and assumptions that are not apparently linked, the same forms of the entropy are obtained to express nonadditivity. It would be extremely interesting to determine if the nonadditivity introduced by Tsallis involves the form of the state functions that we propose, namely, Euler's functions of order  $m$  toward mass, where  $m$  is a number other than 1.

**(II.3) Pressure and Chemical Potential.** The same type of logic of consistency will be applied to pressure. As the temperature is conventionally defined as an intensive variable, the pressure relative to the dimension content is not necessarily nonintensive. Indeed, for dimension content, the pressure is defined as the derivative of a homogeneous function of order  $m$  and a homogeneous function of order 1 (i.e., an extensive function as  $m = 1$ ).

$${}^D P = - \left( \frac{\partial {}^D U}{\partial {}^D V} \right)_{D S, D n_1, D n_2, \chi} \quad (46)$$

The pressure  ${}^D P$  is thus a Euler's function of order  $m - 1$  toward the dimension content. If  $m > 1$ , the pressure  ${}^D P$  decreases with the nonextensive content, whereas, if  $m < 1$ , it increases. The pressure  ${}^D P$  is different from the pressure  $P$ , relative to the extensive content, defined by

$$P = - \left( \frac{\partial {}^E U}{\partial {}^E V} \right)_{E S, E n_1, E n_2} = - \left( \frac{\partial U}{\partial V} \right)_{S, n_1, n_2, \chi} \quad (47)$$

The result is that, for a system at equilibrium, two pressures can be defined depending on whether extensive or dimension contents are considered.

The same applies to the chemical potentials of 1 and 2,  ${}^D \mu_1$  and  ${}^D \mu_2$ , which result from the derivative of a nonextensive function with a dimension variable.

$${}^D \mu_1 = \left( \frac{\partial {}^D U}{\partial {}^D n_1} \right)_{D S, D V, D n_2, \chi} \quad (48)$$

$${}^D \mu_2 = \left( \frac{\partial {}^D U}{\partial {}^D n_2} \right)_{D S, D V, D n_1, \chi} \quad (48')$$

Chemical potentials of components relative to the dimension content of a system depend on this content by a homogeneous function of order  $m - 1$ . Nonintensive properties of chemical potentials and of the pressure can be associated by ensuring that the consistency of eq 21 must be maintained, so

$$dU = d^E U + d^D U = T dS - P dV + \mu_1 dn_1 + \mu_2 dn_2 + \tau d\chi \quad (49)$$

Developing the different terms, this leads to

$$dU = T(d^E S + d^D S) - P d^E V - {}^D P d^D V + {}^E \mu_1 d^E n_1 + {}^D \mu_1 d^D n_1 + {}^E \mu_2 d^E n_2 + {}^D \mu_2 d^D n_2 + \tau d\chi \quad (50)$$

As the temperature is intensive and the volume is extensive, the identification of the various terms leads to

$$dS = d^E S + d^D S \quad (51)$$

$$dV = d^E V + d^D V \quad (52)$$

$$d^E V = V'_1 d^E n_1 + V'_2 d^E n_2 \quad (52')$$

$$d^D V = V'_1 d^D n_1 + V'_2 d^D n_2 \quad (53)$$

A relation between the pressure and chemical potentials relative to the extensive and dimension contents of the system can then be deduced

$${}^D \mu_1 = \mu_1 + V'_1 ({}^D P - P) \quad (54)$$

$${}^D \mu_2 = \mu_2 + V'_2 ({}^D P - P) \quad (54')$$

Chemists can apply these relations, and the Marcelin–De Donder relationship, to the chemical affinity to clarify the evolution conditions of the systems, or to explain the kinetics of reactions.

**(III) Application to Chemical Reactivity.** Properties of homogeneous functions can be used to give simple and easily usable shapes to the expression of chemical potentials.

The first approach is to link the pressure variations to the variables of dimension. For this, a fictitious frontier can be proposed between extensive and dimension contents without changing their state. With the system being at equilibrium, the sum of resulting works has to be null. Therefore,

$$-P d^E V - {}^D P d^D V + \tau d\chi = 0 \quad (55)$$

Suppose that  ${}^D V$  increases. Moving the frontier involves

$$d^D V = -d^E V \quad (56)$$

and as the state of the system remains the same,

$${}^D P - P = \tau \frac{d\chi}{d^D V} \quad (57)$$

The value of the ratio  $(d\chi/d^D V)$  fixes the way in which dimensions of the system evolve in the transformation. This equation can also be explained by noting that the variables  $\chi$  and  ${}^D V$  are homogeneous functions of different orders of the same dimension content. This implies that  $\chi$  is a homogeneous

function of order  $m$  toward  ${}^D V$ , which is expressed by the relationship

$$m\chi = \frac{d\chi}{d{}^D V} {}^D V \quad (58)$$

and for the pressure difference

$${}^D P - P = \tau \frac{d\chi}{d{}^D V} = m \frac{\tau\chi}{{}^D V} = m \frac{E_d}{{}^D V} \quad (59)$$

In this last relation, the energy associated to the variable of dimension  $E_d$  explicitly appears. A general relation which links chemical potentials of the dimension contents to variables of dimension and the degree of homogeneity,  $m$ , is then established.

$${}^D \mu_1 = \mu_1 + V'_1 m \frac{\tau\chi({}^D n_1, {}^D n_2)}{{}^D V({}^D n_1, {}^D n_2)} = \mu_1 + V'_1 m \frac{E_d({}^D n_1, {}^D n_2)}{{}^D V({}^D n_1, {}^D n_2)} \quad (60)$$

$${}^D \mu_2 = \mu_2 + V'_2 m \frac{\tau\chi({}^D n_1, {}^D n_2)}{{}^D V({}^D n_1, {}^D n_2)} = \mu_2 + V'_2 m \frac{E_d({}^D n_1, {}^D n_2)}{{}^D V({}^D n_1, {}^D n_2)} \quad (60')$$

These relationships can only be applied if the dimension content is specified for the system. This is the most delicate issue when using these relations because the extent has been defined as a mainly formal quantity: a justified hypothesis about the nature of this content has to be introduced. Let us take the following examples.

First, consider the simple and unambiguous case of a small aggregate whose content is supposed to be nonextensive, because, according to Defay, it is a limited phase. It could be a small liquid drop or a solid crystal. The parameter of dimension  $\chi$  has to be chosen to be relevant to describe the system behavior, and the way in which this parameter varies with the content of the limited phase has to be identified. This operation is not straightforward, and there may be no single answer. Let us suppose, for instance, that the variable of area is introduced to describe the behavior of a spherical system. This area is a homogeneous function of order  $2/3$  of its content. The tension variable,  $\tau$ , is the interfacial tension,  $\gamma$ .

The application of eq 59 leads to the Laplace law applied to a sphere

$${}^D P - P = \tau m \frac{\chi}{V} = \gamma \frac{2}{3} \frac{A}{V} = \gamma \frac{2}{3} \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \gamma \frac{2}{r} \quad (61)$$

${}^D P$  is the internal pressure of the limited phase, and  $P$ , the pressure of the unlimited phase. The chemical potentials of compounds 1 and 2 are then written as

$${}^D \mu_1 = \mu_1 + V'_1 \frac{2\gamma}{r} \quad (62)$$

$${}^D \mu_2 = \mu_2 + V'_2 \frac{2\gamma}{r} \quad (62')$$

The expression of these magnitudes is similar to the "surface chemical" potential,  $g'_2$ , as reported elsewhere, which permits the equilibrium conditions in a complex system to be described,<sup>19</sup> or this proposed by G. N. Lewis and M. Randall.<sup>2</sup>

These different forms of the chemical potential describe the physicochemical conditions of equilibrium of the system, especially liquid–vapor equilibria. In our example, the liquid

aggregate is at equilibrium with its vapor at fixed total external pressure,  $P$ . Values of affinities of transfer of compounds 1 and 2 from the gas unlimited phase to the limited phase are null.<sup>4</sup>

Thus, for the equilibrium between the solution in the form of the unlimited phase and the vapor phase,

$$\mathcal{A}_1 = \mu_{1\text{liq}} - \mu_{1\text{gas}} = 0 \quad (63)$$

$$\mathcal{A}_2 = \mu_{2\text{liq}} - \mu_{2\text{gas}} = 0 \quad (63')$$

and by developing the terms

$$\mu_{1\text{gas}} = \mu_{1\text{liq}} = \mu_{1\text{gas}}^* + RT \ln\{f_1\} \quad (64)$$

$\mu_{1\text{gas}}^*$  is the standard chemical potential of the gas referred to the perfect gas behavior,  $\{f_1\}$  is the fugacity value of compound 1 in the gas form, and  $\mu_{1\text{liq}}$  is the chemical potential of 1 in solution.

Now, if we consider the case in which the solution is dispersed, the equilibrium condition will be written as

$$\mathcal{A}_1 = {}^D \mu_{1\text{liq}} - \mu_{1\text{gas}} = 0 \quad (65)$$

$$\mathcal{A}_2 = {}^D \mu_{2\text{liq}} - \mu_{2\text{gas}} = 0 \quad (65')$$

so

$$\mu_{1\text{gas}} = \mu_{1\text{liq}} + V'_1 ({}^D P - P) = \mu_{1\text{gas}}^* + RT \ln\{f'_1\} \quad (66)$$

$\{f'_1\}$  is the new fugacity value of the vapor at equilibrium with the solution in spherical drop form. These two values of fugacity are linked by

$$\ln \frac{f'_1}{f_1} = \frac{V'_1}{RT} ({}^D P - P) = \frac{V'_1}{RT} \tau \frac{d\chi}{d{}^D V} = \frac{V'_1}{RT} m \frac{\tau\chi}{{}^D V} \quad (67)$$

The term  $\ln(f'_1/f_1)$  is a homogeneous function of order  $m - 1$  with respect to aggregate mass.

Variations of  $\chi$  and of  $m$  can be determined from experimental values of the ratio  $(f'_1/f_1)$  and the mass of the aggregate.

In the case of a spherical drop of liquid whose radius increases with the mass,  $m = 2/3$  and the application of eq 67 will lead to Kelvin's relationship

$$\ln \frac{f'_1}{f_1} = \frac{V'_1 \gamma}{RT} \frac{2}{r} \quad (68)$$

This kind of demonstration can be applied for other equilibria such as solubility, partition coefficient, or redox potential.

In this example, the extensive content is easily distinguished from the dimension content of the system. This is not the case in complex systems such as micellar systems, interpenetrated media, and others. For data analysis, the problem will be the choice of the variable that is representative of the nonextensive contribution. For systems containing surfactant, for instance, the aggregated surfactant could be considered to be a dimension content and attempts made to determine whether the system behavior can be described from a homogeneous function of order  $m$  with respect to surfactant aggregate. We have proposed this development to explain micellar catalysis.<sup>21,22</sup> This approach involves the Marcelin–De Donder relationship to express the reaction rate.

Consider the equilibrated reaction  $A = B$  in a nonextensive environment. The rate of this reaction can be expressed by the Marcelin–De Donder relationship which includes the chemical

potentials of species in the nonextensive system at instant  $t$  and those at equilibrium. The rate,  $\nu$ , is then written as

$$\begin{aligned}\nu &= \nu^o \left[ \exp\left(\frac{{}^D\mu_A - {}^D\mu_{\text{Aeq}}}{RT}\right) - \exp\left(\frac{{}^D\mu_B - {}^D\mu_{\text{Beq}}}{RT}\right) \right] \\ &= \nu^o \left[ \exp\left(\frac{\mu_A - \mu_{\text{Aeq}}}{RT}\right) \exp\left(\frac{V_A({}^D P - {}^D P_{\text{eq}})}{RT}\right) - \right. \\ &\quad \left. \exp\left(\frac{\mu_B - \mu_{\text{Beq}}}{RT}\right) \exp\left(\frac{V_B({}^D P - {}^D P_{\text{eq}})}{RT}\right) \right] \quad (69)\end{aligned}$$

$\nu^o$  is the exchange rate at equilibrium.

This relationship can be also written as

$$\nu = \nu^o \left[ \exp\left(\frac{\mu_A - \mu_{\text{Aeq}}}{RT}\right) \varphi_A - \exp\left(\frac{\mu_B - \mu_{\text{Beq}}}{RT}\right) \varphi_B \right] \quad (70)$$

The terms  $\varphi_A$  et  $\varphi_B$  are coefficients linked to system dimensions which increase or decrease the “forward” and “reverse” rates of the reaction according to their values. For very high values of  $\varphi_A$ , “direct catalysis” is observed. For very high values of  $\varphi_B$ , the back rate will increase, leading to “reverse catalysis”. This equation has been discussed by T. De Donder<sup>23</sup> and R. Defay<sup>3</sup> for the case of interfacial properties. For the dimension variable  $\chi$ , by combining with eq 59,

$$\ln \varphi_A = \frac{V_A({}^D P - {}^D P_{\text{eq}})}{RT} = \frac{m V_A E_d - E_{d(\text{eq})}}{RT} \quad (71)$$

The catalytic effect occurs only if the value of energy,  $E_d$ , changes with the time of the reaction.

The  $m$  values can be determined from the reaction rates. Thus, we have shown that, in the case of nucleophilic addition of  $\text{OH}^-$  to trinitrobenzene in micellar aqueous solutions, the system behavior can be described by a homogeneous function of order  $m > 1$  ( $m = 1.38$  for DTABr and  $m = 1.75$  for Brij 35).

## Conclusion

New complex reaction media constituted of “nanophases” dispersed in liquids (such as micelles and microemulsions), of interpenetrated domains (bicontinuous media), or even substrates of nanoscopic sizes (nanomaterials), raise the issue of the effects of the sizes and shapes of the reagents and the products on the chemical reactivity. We show here that these variables can be included in assessments if nonextensive terms are introduced into the state functions and considered as Euler’s functions of mass, of a degree of homogeneity other than 1. This implies going outside of the strict framework of thermodynamics.

The relationships proposed in this “nonextensive thermodynamic approach to reactivity” present the advantage of state functions and of their derivatives retaining continuity toward the variables of state, and particularly of temperature respecting its rule of tension extent being identical at all points of the system, equal to that of the reservoir. The behavior of the medium and the chemical reactivity can be described by nonintensive variables (pressure and chemical potential), which depend on the dimension content of the system. Nonextensive functions can obviously be applied to the description of equilibrium conditions but also to reaction kinetics in dispersed systems.

Particular attention must be given to the fact that, in the case of nonextensive functions of state, the additivity property is not valid, especially when the entropy is concerned. This property has been introduced and developed by numerous physicists, particularly by C. Tsallis, using statistical approaches. This

approach is still the subject of debate and controversy. Various fundamental aspects of the relation between the statistical mechanics and thermodynamics remain obscure. Some analyses show, for example, that transformations of appropriate variables<sup>13</sup> can account for the nonextensive thermodynamics of C. Tsallis within classical extensive thermodynamics. Furthermore, the relations between microscopic and macroscopic magnitudes are not clear. For example, C. Tsallis et al. noted that, in the microscopic state, the internal energy can behave as a nonextensive extent, but in the macroscopic state, this extent becomes extensive. The difference of behavior between macroscopic internal energy and macroscopic entropy is justified by these authors by saying that entropy is linked to a “quantity of information” and that internal energy is linked to a “mechanical quantity”.<sup>10</sup> S. Abe recently showed that macroscopic entropy must be extensive, even if in the microscopic state it could be nonextensive.<sup>15</sup> In a recent paper, H. Touchette specified the sense of the two terms additivity and extensivity and showed that “it is sometimes possible to transform a nonextensive quantity into an extensive one by rescaling it...by dividing the quantity in question by its nonlinear scaling law....”<sup>24</sup>

We do not enter into these discussions, but we will simply note that by a totally different approach we characterize the nonadditivity of macroscopic entropy by relations with forms similar to those proposed by C. Tsallis. It is interesting to consider the possible relations between these two approaches and especially the properties of the form of macroscopic internal energy that we have also, in this work, assumed to be nonextensive.

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