

THE QUANTUM EXPRESSION FOR ENTROPY

Erol Çubukçu

Department of Nuclear Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Elias P. Gyftopoulos

Departments of Mechanical Engineering
and of Nuclear Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

ABSTRACT

Numerous expressions exist in the scientific literature purporting to represent entropy. Are they all acceptable? To answer this question, we review the thermodynamic definition of entropy, and establish eight criteria that must be satisfied by it. The definition and criteria are obtained by using solely the general, nonstatistical statements of the first and second laws presented in *Thermodynamics: Foundations and Applications* by Gyftopoulos and Beretta (1991).

We apply the eight criteria to each of the expressions proposed in the literature and, for the first time, find that only the relation $S = -kTr\rho \ln\rho$ satisfies all the criteria, provided that the density operator ρ corresponds to a homogeneous ensemble of identical systems, identically prepared. Homogeneous ensemble means that every member of the ensemble is described by the same density operator ρ as any other member, that is, the ensemble is not a statistical mixture of projectors (wave functions).

NOMENCLATURE

A a system
 A_i i th state of system A
 a acceleration
 B a system
 B_i i th state of system B
 C a composite of two subsystems A and B
 c_R positive constant that depends on the reservoir R only
 E energy
 E_g lowest energy for which a system with given values of n and V can exist
 E_i energy of i th state of system A
 $E(t_i)$ energy of system A at time t_i

E^{X-} energy transferred from the environment to system X; positive if transfer is into system X, and negative if transfer is out of system X
 F force
 g gravitational acceleration
 H Hamiltonian operator
 \hbar Planck's constant h divided by 2π
 k Boltzmann's constant
 M mass of a weight
 m mass
 $N(\rho)$ number of positive eigenvalues of ρ
 n vector of amounts of r constituents
 p_i probability of i th condition
 $p_{largest}$ largest eigenvalue of density operator ρ
 R a reservoir
 S entropy
 S_D Daróczy entropy
 S_H Hartley entropy
 S_i entropy of i th state of system A
 S_∞ infinite norm entropy
 S_{irr} entropy generated spontaneously within a system; it is nonnegative
 S_R Renyi entropy
 S_v von Neumann entropy
 S^{X-} entropy transferred from the environment to system X; positive if transfer is into system X, and negative if transfer is out of system X
 T temperature
 T_g temperature of any ground-energy state
 t, t_i time
 V volume

z_i	elevation of point i in a gravity field
α	a positive constant different from unity
β	vector of values of s parameters
e	energy eigenvalue of a two-energy level system (spin)
ρ	density operator that corresponds to a homogeneous ensemble of identical systems, identically prepared; it is not a mixture of projectors (wave functions)
$\ \rho\ _\infty$	the largest eigenvalue of ρ
Ψ	generalized adiabatic availability
Ω^R	generalized available energy of system A with respect to a given auxiliary reservoir R
Ω_i^R	generalized available energy of the i th state of system A with respect to a given auxiliary reservoir R

INTRODUCTION

In his authoritative review "General properties of entropy," Wehrl (1978) writes: "It is paradoxical that although entropy is one of the most important quantities of physics, its main properties are rarely listed in the usual textbooks on statistical mechanics." We concur fully with this assessment, and add that the main characteristics of entropy are rarely listed even in the usual textbooks on thermodynamics, despite the fact that entropy is clearly a thermodynamic (not mechanical) concept.

The lack of specificity has resulted in a plethora of expressions purporting to represent the entropy of thermodynamics, and perhaps influenced von Neumann to respond to Shannon's question "What should I call $-\sum_i p_i \ln p_i$?" by saying "You should call it 'entropy' for two reasons: first, the function is already in use in thermodynamics under that name; second, and more importantly, most people don't know what entropy really is, and if you use the word entropy you will win every time!" (Tribus, 1963).

The purposes of this paper are to redress the omissions, and to prove that, as a well-defined property of matter, entropy is represented only by the quantum-theoretic functional $S = -k\text{Tr}\rho \ln \rho$. Even though the expression is very well known and more often than not rejected in statistical quantum mechanics, here the proof is solely thermodynamic and novel.

The paper is organized as follows. In the second section we provide a general thermodynamic definition of entropy for any system (large or small) in any state (thermodynamic equilibrium or not thermodynamic equilibrium). In the third section we list eight sensible characteristics of this entropy which can be used as criteria of acceptance of any analytic expression purporting to represent entropy. In the fourth section we summarize a number of quantum expressions for entropy that have appeared in the literature, and investigate whether one or more of these expressions conform with the eight criteria listed in the preceding section.

As a result of this investigation, for the first time we prove that only the expression $S = -k\text{Tr}\rho \ln \rho$ conforms with all the criteria, provided that the density operator ρ represents the quantum-theoretic probabilities derivable from a homogeneous ensemble of identical systems, identically prepared.

The homogeneous ensemble is a generalization of the concept introduced by von Neumann (1955). It is an ensemble of identical members in which each member is described by the same density operator ρ ($\rho \geq \rho^2$) as any other member, that is, the ensemble is not a statistical mixture of projectors (wave functions). In other words, physically as opposed to algebraically, the density operator compatible with thermodynamics is the seat of quantum-theoretic probabilities only, and not a mixture of quantum probabilities derived from projectors, and classical statistical probabilities introduced because of either ignorance or lack of interest in the details of the system, or both.

GENERAL THERMODYNAMIC DEFINITION OF ENTROPY

A system A in any state A_1 has many properties. Two of these properties are: energy E_1 , and generalized available energy Ω_1^R with respect to a given auxiliary reservoir R (the definitions of energy and generalized available energy are briefly discussed in the Appendix). Complete proofs of each and every statement in both this and the next section are provided in Gyftopoulos and Beretta (1991).

Energy and generalized available energy determine a third property called *entropy*, and denoted by the symbol S . It is a property in the same sense that energy is a property, or momentum is a property. For a state A_1 , S_1 can be evaluated by means of an auxiliary reservoir R , a reference state A_0 , with energy E_0 and generalized available energy Ω_0^R , to which is assigned a reference value S_0 , and the expression

$$S_1 = S_0 + \frac{1}{c_R} \left[(E_1 - E_0) - (\Omega_1^R - \Omega_0^R) \right] \quad (1)$$

where c_R is a well-defined positive constant that depends on the auxiliary reservoir R only. Entropy S is shown to be independent of the reservoir, that is, indeed the reservoir is auxiliary and is used only because it facilitates the definition of S . It is also shown that S can be assigned absolute values that are nonnegative, and that vanish for all the states encountered in mechanics.

The concept of entropy introduced here differs from and is more general than that of most textbooks. It does not involve the concepts of temperature and heat; it is not restricted to large systems; it applies to macroscopic as well as microscopic systems, including a system with one spin, or a system with one particle with only one (translational) degree of freedom; it is not restricted to stable (thermodynamic) equilibrium states; it is defined for both stable equilibrium and not stable

(thermodynamic) equilibrium states because energy and generalized available energy are defined for all states; and most certainly, it is not statistical — it is a property of matter. To emphasize the difference and generality of the concept, we recall contrary statements by Meixner (1970), "A careful study of the thermodynamics of electrical networks has given considerable insight into these problems and also produced a very interesting result: the nonexistence of a unique entropy value in a state which is obtained during an irreversible process,...., I would say I have done away with entropy," and Callen (1985), "it must be stressed that we postulate the existence of the entropy only for equilibrium states and that our postulate makes no reference whatsoever to nonequilibrium states."

Like energy, entropy is an additive property. Whereas energy remains constant in time if the system experiences either a spontaneous process or a zero-net-effect mechanical interaction, it is shown that the entropy defined by equation (1) remains constant if either of these processes is reversible, and increases if either of these processes is irreversible. These features are known as *the principle of nondecrease of entropy*. A process is reversible if both the system and its environment can be restored to their respective initial states. A process is irreversible if the restoration just cited is impossible.

The entropy created as time proceeds during an irreversible process is called *entropy generated by irreversibility*. It is positive. The entropy nondecrease is a time-dependent result. Here it is obtained without use of the general equation of motion.

Like energy, entropy can be transferred between systems by means of interactions. Denoting by S^{A^-} the amount of entropy transferred from systems in the environment to system A as a result of all interactions involved in a process in which the state of A changes from A_1 to A_2 , we derive a very important analytical tool, the *entropy balance*, that is,

$$(S_2 - S_1)_{\text{system A}} = S^{A^-} + S_{\text{irr}} \quad (2)$$

where S_{irr} is positive or at least zero and represents the entropy generated spontaneously within system A during the time interval from t_1 to t_2 required to affect the change from state A_1 to state A_2 . Spontaneous entropy generation within a system occurs if the system is in a nonequilibrium state in which the internal dynamics precipitate the natural tendency towards stable equilibrium.

The dimensions of S depend on the dimensions of both energy and c_R . It turns out that the dimensions of c_R are independent of mechanical dimensions, and are the same as those of temperature.

GENERAL CHARACTERISTICS OF ENTROPY

From the discussions in the preceding section and the Appendix, we conclude that any expression that purports to represent the entropy of thermodynamics must have at least the following eight characteristics or, equivalently, conform to the following eight criteria.

1. The expression must be well defined for every system (large or small), and every state (stable equilibrium or not stable equilibrium).
2. The expression must be invariant in all reversible adiabatic processes, and increase in any irreversible adiabatic process.
3. The expression must be additive for all systems and all states.
4. The expression must be nonnegative, and vanish for all the states encountered in mechanics.
5. For given values of energy, amounts of constituents, and parameters, one and only one state must correspond to the largest value of the expression.
6. For given values of the amounts of constituents and parameters, the graph of energy versus entropy of stable equilibrium states must be convex and smooth. Equivalently, the fundamental relation entropy versus energy must be concave and smooth.
7. For a composite C of two subsystems A and B, the expression must be such that the entropy maximization procedure for C (criterion no. 5) yields identical thermodynamic potentials (for example, temperature, chemical potentials, and pressure) for all three systems A, B, and C.
8. For stable equilibrium states, the expression must reduce to relations that have been established experimentally and that express the entropy in terms of the values of energy, amounts of constituents, and parameters.

QUANTUM EXPRESSIONS FOR ENTROPY

Ever since the enunciation of the first and second laws of thermodynamics by Clausius about 130 years ago, all expressions for entropy that are not based on temperature and heat involve probabilities. Invariably, the probabilities are statistical (as opposed to inherent to the nature of physical phenomena), and are introduced as a means to partially overcome the enormous computational and informational difficulties resulting from the complexity of the "actual state" (classical or quantum) of a large system. Thus, each expression of entropy is usually construed as a subjective measure of information rather than an analytical description of an objective property of matter.

Over the past two decades, a different point of view has been developed consistent with the idea that entropy is a property of matter. Hatsopoulos and Gyftopoulos (1976d) observed that the von Neumann concept of a homogeneous ensemble of identical systems that represents a projector (every member of the ensemble is described by the same projector, $\rho = \rho^2$, or wave function as any other member) can be readily extended to density operators (every member of the ensemble is described by the same density operator, $\rho > \rho^2$, as any other member, that is, the ensemble is not a statistical mixture of projectors). This extension is accomplished without any changes of the quantum-theoretic postulates about observables, measurement results, and values of observables. An identical conclusion is reached by other scientists (Jauch, 1968).

TABLE 1

ENTROPY EXPRESSION	CRITERION							
	1	2	3	4	5	6	7	8
S_D	Y ¹	Y	N ²	—	—	—	—	—
S_H	Y	Y	Y	Y	N	—	—	—
S_∞	Y	Y	Y	Y	Y	N	—	—
S_R	Y	Y	Y	Y	Y	Y	N	—
S_v	Y	Y	Y	Y	Y	Y	Y	Y

¹Y Criterion is satisfied

²N Criterion is not satisfied

One benefit of the observation just cited is the elimination of the monstrosity of the concept of mixed state that concerned Schroedinger (1936) and Park (1968, 1988).

Another even more important benefit is that the extension results in a unified quantum theory which encompasses within a single structure of concepts and mathematical representatives both mechanics and thermodynamics without any need for statistical (subjective or informational) probabilities (Hatsopoulos and Gyftopoulos, 1976a,b,c). The unified theory applies to all systems, small or large, including a one spin system, and all states, unsteady, steady, nonequilibrium, equilibrium, and stable (thermodynamic) equilibrium.

Next, Hatsopoulos and Gyftopoulos postulated that the special class of unitary transformations of ρ with respect to time obey the von Neumann equation of motion

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] \quad (3)$$

for both isolated systems (Hamiltonian operators H independent of time), and nonisolated systems (Hamiltonian operators H explicitly dependent on time). It is noteworthy that equation (3) must be introduced as a postulate because it cannot be derived from the Schroedinger equation since ρ is not a mixture of wave functions.

As it is well known, the processes described by equation (3) are reversible adiabatic. However, neither all reversible adiabatic processes correspond to unitary transformations of ρ with respect to time, nor all adiabatic processes are reversible. Accordingly, as an equation of motion of physics, equation (3) is incomplete.¹ Its completion is one of the most challenging outstanding problems of contemporary physics.

¹Many efforts have been made to complete the equation of motion. For comments and concrete results see Wehrl (1978), Hatsopoulos and Gyftopoulos (1976a,b,c,d), Park and Simmons (1983), Beretta et al. (1984, 1985), Korsch and Steffen (1987), Lindblad (1976), and Çubukçu (1993).

If there exist constants of the motions of all the reversible adiabatic processes described by equation (3), Hatsopoulos and Gyftopoulos (1976a,b,c) concluded that each such constant must be a functional solely of the eigenvalues of ρ because these are the only quantities that remain invariant in the course of all unitary transformations with respect to time.

In the light of the new point of view, and the eight criteria of the preceding section, we conclude that: (a) expressions for entropy based on temperature and heat are not acceptable because they are restricted to thermodynamic equilibrium states only; (b) expressions for entropy proposed in statistical classical mechanics are not acceptable because they are based on statistical (subjective) rather than quantal (inherent) probabilities, and the resulting entropy is not a property of matter; and (c) expressions for entropy proposed in statistical quantum mechanics (Tolman, 1962; Jancel, 1969) that depend on variables other than the eigenvalues of ρ are not acceptable because they fail criterion 2 for processes in which the changes of ρ are unitary. Some quantum functionals that are proposed in the literature, and that are candidates as possible expressions for entropy are the following.

The Daróczy entropy (Daróczy, 1970)

$$S_D = \frac{1}{2^{1-\alpha} - 1} (\text{Tr} \rho^\alpha - 1) \quad (4)$$

where $\alpha > 0$, $\alpha \neq 1$.

The Hartley entropy (Hartley, 1928)

$$S_H = k \ln N(\rho) \quad (5)$$

where $N(\rho)$ is the number of positive eigenvalues of ρ .

The infinite norm entropy

$$S_{\infty} = -k \ln \|\rho\|_{\infty} \quad (6)$$

where $\|\rho\|_{\infty} = P_{\text{largest}}$ = the largest eigenvalue of ρ .

The Rényi entropy (Rényi, 1966)

$$S_R = \frac{k}{1-\alpha} \ln(\text{Tr} \rho^{\alpha}) \quad (7)$$

where $\alpha > 0$, $\alpha \neq 1$.

The von Neumann entropy (von Neumann, 1929)

$$S_v = -k \text{Tr} \rho \ln \rho \quad (8)$$

Applying criteria 1 to 8 of the preceding section to expressions 4 to 8, we find the results listed in Table 1.

Specifically, the Daróczy entropy satisfies criteria 1 and 2 but fails criterion 3 — is not additive. Accordingly, S_D is not acceptable as an expression for entropy.

The Hartley entropy satisfies criteria 1 to 4 but fails criterion 5. For given values of energy E , amounts of constituents n , and parameters β , many density operators have the same number of positive eigenvalues as the density operator that corresponds to the unique stable equilibrium state associated with E , n , β . It follows that the Hartley entropy is not acceptable.

It can be easily shown that the infinite norm entropy conforms to criteria 1 to 5 (Çubukçu, 1993). To probe criterion 6, we consider a system that has only two energy eigenvalues, $-e$ and $+e$ (spin system). For this system and a given value of the energy E , we can show (Çubukçu, 1993) that the largest eigenvalue, P_{largest} of the density operator of the corresponding stable equilibrium state satisfies the relation

$$P_{\text{largest}} = \frac{1}{2} \left(1 \pm \frac{E}{e} \right) \quad (9)$$

where the $+$ sign applies if $E > 0$, and $-$ sign if $E < 0$. Thus, the E versus S graph is neither convex nor smooth as required by the laws of thermodynamics (criterion 6). It is concave both in the positive and the negative temperature ranges. Accordingly, the infinite norm entropy is not acceptable.

Next, we can show that the Rényi entropy satisfies criteria 1 to 6 but fails criterion 7 (Çubukçu, 1993). All the proofs are straightforward, but some are algebraically lengthy and are not repeated here. So the Rényi entropy is not acceptable.

The von Neumann entropy satisfies all the criteria 1 to 8. So, it is the only known quantum expression of entropy that is acceptable.

Because the von Neumann entropy appears in practically every textbook on statistical quantum mechanics, some

additional remarks are necessary here. In statistical quantum mechanics, several different derivations of S_v are given (Tolman, 1962; Jaynes, 1957; Aczél et al., 1974; Ochs, 1975). Each of these derivations, however, introduces hypotheses or axioms which are not consistent with the idea that entropy is a property of matter. For example, von Neumann's derivation (Tolman, 1962; von Neumann, 1929) is based on the premise of mixing pure states (projectors). Such a premise leads to contradictions (Hatsopoulos and Gyftopoulos, 1976d; Park and Simmons, 1983). Again, Ochs' derivation (Ochs, 1975) is based on the assumptions that the expression for entropy must satisfy the conditions of "partial isometric invariance" and "subadditivity," conditions which are not justified by the laws of thermodynamics.

The first proof that S_v is the quantum expression for entropy is given by Hatsopoulos and Gyftopoulos (1976a,b,c). However, certain features of their derivation are mathematically faulty. So, the conclusion that S_v is the only known quantum expression for entropy is a novel result presented here for the first time.

CLOSING REMARK

In addition to shedding some light on the meaning of entropy as a property of matter, density operators that satisfy the relation $\rho \geq \rho^2$, and that cannot be physically (as opposed to numerically) decomposed into mixtures of pure states open several interesting questions at the frontier of contemporary physics. Both from the theoretical and the engineering points of view, the most important of these questions relates to the form of the complete equation of motion, the equation that applies to all reversible adiabatic processes, and to all irreversible processes.

APPENDIX: THERMODYNAMICS

General remarks

We include this appendix because the definition of entropy we use in this paper is not well known.

Many scientists and engineers have expressed concerns about the completeness and clarity of the usual expositions of thermodynamics. For example, in the preface of his book *Concepts of Thermodynamics*, Obert (1960) writes: "Most students will agree that the subject of engineering thermodynamics is confusing to the student despite the simplicity of the usual undergraduate presentation." Again, Tisza (1970) states: "The motivation for choosing a point of departure for a derivation is evidently subject to more ambiguity than the technicalities of the derivation...In contrast to errors in experimental and mathematical techniques, awkward and incorrect points of departure have a chance to survive for a long time." And again, in their textbook, Gyftopoulos and Beretta (1991) comment: "In our experience, the major source of confusion is the lack of logical consistency and completeness in the many presentations of the foundations of thermodynamics.

The definition of a system as just the 'subject of analysis' or 'anything that is enclosed by a surface in space' is incomplete. The definition of properties in terms of the state is circular if the definition of state is in terms of the properties. The definition of heat as anything that is not work (or the energy exchanged across a temperature difference) is incomplete and ambiguous. The definition of thermal equilibrium in terms of temperature is circular if the definition of temperature is in terms of thermal equilibrium. The restriction to equilibrium states is artificial if the purpose is the use of heat and cycles to define entropy. Even if entirely uninterested in the foundations, the student cannot avoid but sense this ambiguity and lack of logical consistency and develop the incorrect conviction that thermodynamics is a confusing, ambiguous, hand-waving subject. Unfortunately, such a conviction is quite widespread..."

In response to numerous such concerns, Gyftopoulos and Beretta (1991) have composed a novel exposition in which all basic concepts of thermodynamics are defined completely and without circular arguments in terms of well known mechanical ideas. Many of these definitions are new.

The order of introduction of concepts and principles is: system (types and amounts of constituents, forces between constituents, and external forces or parameters); properties; states; the first law; energy (without work and heat); energy balance; classification of states in terms of time evolutions; stable equilibrium states; second law (without temperature, heat, and entropy); generalized available energy; entropy of any state, stable equilibrium or not, in terms of energy and generalized available energy and not in terms of temperature and heat; entropy balance; fundamental relation for stable equilibrium states only; temperature, total potentials, and pressure in terms of energy, entropy, amounts of constituents and parameters for stable equilibrium states only; the third law; work in terms of energy; heat in terms of energy, entropy, and temperature; and graphical representations of results on an energy versus entropy plane.

All concepts and principles are valid for all systems (macroscopic or microscopic), and all states (thermodynamic or stable equilibrium or not stable equilibrium).

To facilitate the reading of this paper, in what follows we repeat briefly some of the concepts. For a comprehensive discussion we refer the reader to Gyftopoulos and Beretta (1991).

General Thermodynamics

We define general thermodynamics or simply thermodynamics as the study of motions of physical constituents (particles and radiations) resulting from externally applied forces, and from internal forces (the actions and reactions between constituents). This definition is identical to that given by Timoshenko and Young (1948) about mechanical dynamics. However, because of the second law, the definition encompasses a much broader spectrum of phenomena than mechanical dynamics.

Kinematics: Conditions at an Instant of Time

In kinematics we give verbal definitions of the terms system, property, and state so that each definition is valid without change in any physical theory, and involves no statistics attributable to lack of information. The definitions include innovations. To the best of our knowledge, they violate no theoretical principle and no experimental result.

A *system* is defined as a collection of *constituents* subject to *internal intermolecular forces* and *external forces*.

Everything that is not included in the system is the *environment*.

For a system with r constituents, we denote their amounts by the vector $\mathbf{n} = \{n_1, n_2, \dots, n_r\}$. For a system with external forces described by s parameters we denote the parameters by the vector $\boldsymbol{\beta} = \{\beta_1, \beta_2, \dots, \beta_s\}$. One parameter may be volume, $\beta_1 = V$.

At any instant of time, the amount of each constituent, and the parameters of each external force have specific values. We denote these values by \mathbf{n} and $\boldsymbol{\beta}$ with or without additional subscripts.

By themselves, the values of the amounts of constituents and of the parameters at an instant of time do not suffice to characterize completely the condition of the system at that time. We also need the values of all the properties at the same instant of time. Each *property* is an attribute that can be evaluated at any given instant of time by means of a set of measurements and operations that are performed on the system and result in a numerical value — the *value of the property*. This value is independent of the measuring devices, other systems in the environment, and other instants of time.

For a given system, the values of the amounts of all the constituents, the values of the parameters, and the values of a complete set of independent properties encompass all that can be said about the system at an instant of time and about the results of any measurements that may be performed on the system at that same instant of time. We call this complete characterization of the system at an instant in time the *state* of the system. This definition of state is novel and, without change, applies to any branch of physics.

Dynamics: Changes of State with Time

The state of a system may change with time either spontaneously due to the internal forces or as a result of interactions with other systems, or both.

The relation that describes the evolution of the state of an isolated system — *spontaneous changes of state* — as a function of time is the *equation of motion*. Certain time evolutions obey *Newton's equation* which relates the total force F on each system particle to its mass m and acceleration a so that $F = ma$. Other evolutions obey the *time-dependent Schroedinger equation*, that is, the quantum-mechanical equivalent of Newton's equation. Other experimentally observed time evolutions, however, do not obey either of these equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion

that describes all physical phenomena remains a subject of research at the frontier of science — one of the most intriguing and challenging problems in physics (see footnote 1).

Many features of the equation of motion have already been discovered. These features provide not only guidance for the discovery of the complete equation but also a powerful alternative procedure for analyses of many time-dependent, practical problems. Two of the most general and well-established features are captured by the consequences of the first and second laws of thermodynamics discussed later.

Energy and Energy Balance

Energy is a concept that underlies our understanding of all physical phenomena, yet its meaning is subtle and difficult to grasp. It emerges from a fundamental principle known as the first law of thermodynamics.

The *first law* asserts that any two states of a system may always be the initial and final states of a change (weight process) that involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight, that is, a mechanical effect. Moreover, for a given weight, the value of the expression $Mg(z_1 - z_2)$ is fixed only by the end states of the system, where M is the mass of the weight, and g the gravitational acceleration.

The main consequence of this law is that every system A in any state A_1 has a property called *energy*, with a value denoted by the symbol E_1 . The energy E_1 can be evaluated by a weight process that connects A_1 and a reference state A_0 to which is assigned an arbitrary reference value E_0 so that

$$E_1 = E_0 - Mg(z_1 - z_0) \quad (10)$$

Energy is an additive property, that is, the energy of a composite system is the sum of the energies of its subsystems. Moreover, energy has the same value at the final time as at the initial time if the system experiences a zero-net-effect weight process, or remains invariant in time if the process is spontaneous. In either of the last two processes, $z_2 = z_1$ and $E(t_2) = E(t_1)$ for time t_2 greater than t_1 , that is, energy is *conserved*. Energy conservation is a time-dependent result. Here it is obtained without use of the general equation of motion.

Energy can be transferred between systems by means of interactions. Denoting by E^{A-} the amount of energy transferred from the environment to system A in a process that changes the state of A from A_1 to A_2 , we can derive the *energy balance*. This balance is based on the additivity of energy and energy conservation, and reads

$$(E_2 - E_1)_{\text{system } A} = E^{A-} \quad (11)$$

In words, the energy change of a system must be accounted for by the energy transferred across the boundary of the system.

Types of States

Because the number of independent properties of a system is infinite even for a system consisting of a single particle with a single translational degree of freedom — a single variable that fixes the configuration of the system in space — and because most properties can vary over a range of values, the number of possible states of a system is infinite. The discussion of these states is facilitated if they are classified into different categories according to time evolutions. This classification brings forth many important aspects of physics, and provides a readily understandable motivation for the introduction of the second law of thermodynamics.

The classification consists of: unsteady states; steady states; nonequilibrium states; and equilibrium states. An *equilibrium state* is one that does not change as a function of time while the system is isolated — a state that does not change spontaneously. An *unstable equilibrium state* is an equilibrium state that may be caused to proceed spontaneously to a sequence of entirely different states by means of a minute and short-lived interaction that has only an infinitesimal temporary effect on the state of the environment. A *stable equilibrium state* is an equilibrium state that can be altered to a different state only by interactions that leave net effects in the environment of the system. These definitions are identical to the corresponding definitions in mechanics but include a much broader spectrum of states than those encountered in mechanics. The broader spectrum is due to the second law discussed later.

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, a system can transfer energy out and affect a mechanical effect without leaving any other net changes in the state of the environment. In contrast, experience shows that, starting from a stable equilibrium state, a system cannot affect the mechanical effect just cited. This impossibility is one of the most striking consequences of the first and second laws of thermodynamics. It is consistent with innumerable experiences. The second law is introduced in the next section.

Generalized Available Energy

The existence of stable equilibrium states is not self-evident. It was first recognized by George Nicholas Hatsopoulos and Joseph Henry Keenan (1965) as the essence of all correct statements of the second law. Gyftopoulos and Beretta concur with this recognition, and state the *second law* as follows (simplified version): Among all the states of a system with a given value of energy, and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state.

The existence of stable equilibrium states for the conditions specified and, therefore, the second law cannot be derived from the laws of mechanics. Within mechanics, the stability analysis yields that among all the allowed states of a system with fixed values of amounts of constituents and parameters, the only stable equilibrium state is that of lowest energy. In contrast the second law avers the existence of a stable equilibrium state for each value of the energy. As a result, for every system the

second law implies the existence of a broad class of states in addition to the states contemplated by mechanics.

The existence of stable equilibrium states for various conditions of matter has many theoretical and practical consequences. One consequence is that, starting from a stable equilibrium state of any system, no energy can be used to affect a mechanical effect while the values of the amounts of constituents and parameters of the system experience no net changes. This consequence is often referred to as the impossibility of the perpetual motion machine of the second kind (PMM2). In some expositions of thermodynamics, it is taken as the statement of the second law. In the new exposition, it is only one aspect of both the first and the second laws.

Another consequence is that not all states of a system can be changed to a state of lowest energy by means of a mechanical effect. This is a generalization of the impossibility of a PMM2. In essence, it is shown that a novel important property exists called *generalized adiabatic availability* and denoted by Ψ . The generalized adiabatic availability of a system in a given state represents the optimum amount of energy that can be exchanged between the system and a weight in a weight process. It differs from energy. Like energy, this property is well defined for all systems and all states. Unlike energy it is not additive.

In striving to define an additive property that captures the important features of generalized adiabatic availability, Gyftopoulos and Beretta introduce a special reference system, called a *reservoir*, and discuss the possible weight processes that the composite of a system and the reservoir may experience. Thus, they disclose a third consequence of the first and second laws, that is, a limit on the optimum amount of energy that can be exchanged between a weight and a composite of a system and a reservoir R — the optimum mechanical effect. They call the optimum value *generalized available energy*, denote it by Ω^R , and show that it is additive. It is a generalization of the concept of motive power of fire first introduced by Carnot. It is a generalization because he assumed that both systems of the composite acted as reservoirs with fixed values of their respective amounts of constituents and parameters, whereas Gyftopoulos and Beretta do not use this assumption. The definition of a reservoir is given in Gyftopoulos and Beretta (1991).

In contrast to energy, generalized available energy is conserved in reversible adiabatic processes but decreases in irreversible adiabatic processes.

It is noteworthy that energy and generalized available energy are defined for any state of any system, regardless of whether the state is steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether the size of the system is large or small.

As discussed in the second section of the paper, energy and generalized available energy are used to define entropy.

For discussions of stable equilibrium states, the fundamental relation, temperature, total potentials, pressure, work, and heat see Gyftopoulos and Beretta (1991).

Energy Versus Entropy Graphs

Because they are defined in terms of the values of the amounts of constituents, the parameters, and a complete set of independent properties, states can in principle be represented by points in a multidimensional geometrical space with one axis for each amount, parameter, and independent property. Such a representation, however, would not be enlightening because the number of independent properties is very large. Nevertheless, useful information can be summarized by first cutting the multidimensional space with a surface corresponding to given values of each of the amounts of constituents and each of the parameters, and then projecting the result onto a two-dimensional plane — a plane of two property axes. The energy versus entropy plane is very useful because it illustrates many of the basic concepts of thermodynamics.

We consider a system with volume V as the only parameter, and no upper bound on the value of the energy. For given values of the amounts of constituents and the volume, we project the multi-dimensional state space of the system onto the E versus S plane. This projection includes both stable equilibrium states and other states that are not stable equilibrium. The laws of thermodynamics imply that the projection must have the shape of the cross-hatched area shown in Figure A-1, that is, all the states that share the given characteristics have property values that project on the area between the vertical line denoted as the line of zero-entropy states, and the curve of the stable equilibrium states.

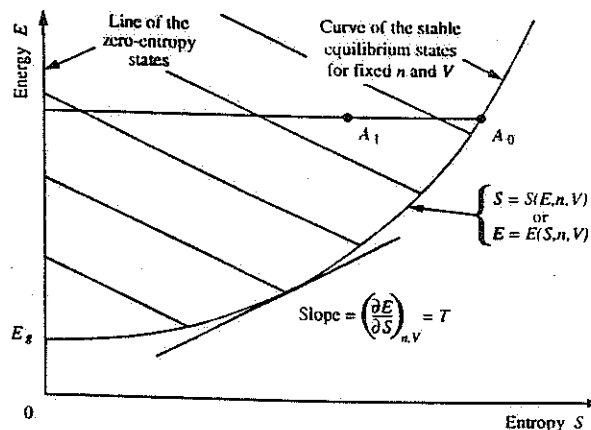


FIGURE A-1

A point either inside the cross-hatched area or on the vertical line $S = 0$ represents a large number of states. Each such state has the same values of amounts of constituents, volume, energy and entropy, but differing values of other properties, and is not a stable equilibrium state. It can be any state except a stable equilibrium state.

A point on the convex curve of stable equilibrium states represents one and only one state. For each of these states, the value of any property is uniquely determined by the values of the amounts of constituents, the volume, and either E or S of the point on the curve.

The zero-entropy states correspond to states contemplated in mechanics. All other states belong to the broad class of nonmechanical states whose existence is implied and required by the second law. So mechanics can be regarded as a special case of thermodynamics — zero-entropy physics.

For the given values n , V , the energy E_g is the lowest energy for which the system can exist. It corresponds to zero entropy and zero temperature. If we were using quantum-theoretical concepts, we would be able to show that all ground-energy states have the same temperature T_g , and that the value of this temperature is equal to zero. Instead, we note that this important conclusion of the quantum-theoretical treatment cannot be drawn as a logical conclusion of the statements of the first and second laws, but here must be presented as an additional fundamental postulate. It is known as the *third law of thermodynamics* or the *Nernst principle* and can be stated as follows. For each given set of values of the amounts of constituents and the parameters of a system, there exists one stable equilibrium state with zero temperature.

The stable-equilibrium-state curve represents the relations $S = S(E, n, V)$ or $E = E(S, n, V)$. Each stable equilibrium state has either the lowest energy for a given entropy, or the highest entropy for a given energy.

Because each stable equilibrium state is unique, the temperature $T = (\partial E / \partial S)_{n, V}$ at each point on the curve. Temperature is not defined for states that are not stable equilibrium because then E , S , n , V are independent and, therefore, the partial derivative of E with respect to S is meaningless.

Starting from a state A_0 , the system cannot transfer energy to affect a mechanical effect without net changes in n and V because no state of lower energy exists that has an entropy equal to or greater than the entropy of A_0 . This is a graphical illustration of the impossibility of PMM2. It is sometimes expressed as the nonexistence of a *Maxwellian demon*. The impossibility does not apply to states, such as A_1 , that are not stable equilibrium.

ACKNOWLEDGEMENT

We are thankful to Dr. George N. Hatsopoulos, CEO and President, Thermo Electron Corporation, for financial support of this work.

REFERENCES

- Aczél, J., Forte, B., and Ng, C. T., 1974, *Advances in Applied Probability*, Vol. 6, p. 131.
- Beretta, G. P., Gyftopoulos, E. P., and Park, J. L., 1985, *Il Nuovo Cimento*, Vol. 87B, 1, p. 77.
- Beretta, G. P., Gyftopoulos, E. P., Park, J. L., and Hatsopoulos, G. N., 1984, *Il Nuovo Cimento*, Vol. 82B, 2, p. 169.
- Callen, H. B., 1985, *Thermodynamics and Introduction to Thermostatistics*, Second Edition, Wiley, p. 27.
- Çubukçu, E., 1993, "Thermodynamics as a Non-Statistical Theory," Ph.D. Thesis, Dept. of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, MA.
- Daróczy, Z., 1970, *Information and Control*, Vol. 16, p. 74.
- Gyftopoulos, E. P., and Beretta, G. P., 1991, *Thermodynamics: Foundations and Applications*, Macmillan, New York.
- Hartley, R. V., 1928, *Bell System Technical Journal*, Vol. 7, p. 535.
- Hatsopoulos, G. N., and Gyftopoulos, E. P., 1976a, *Foundations of Physics*, Vol. 6, 1, p. 15.
- Hatsopoulos, G. N., and Gyftopoulos, E. P., 1976b, *Foundations of Physics*, Vol. 6, 2, p. 127.
- Hatsopoulos, G. N., and Gyftopoulos, E. P., 1976c, *Foundations of Physics*, Vol. 6, 4, p. 439.
- Hatsopoulos, G. N., and Gyftopoulos, E. P., 1976d, *Foundations of Physics*, Vol. 6, 5, p. 561.
- Hatsopoulos, G. N., and Keenan, J. H., 1965, *Principles of General Thermodynamics*, John Wiley, New York.
- Jancel, R., 1969, *Foundations of Classical and Quantum Statistical Mechanics*, Pergamon Press, New York.
- Jauch, J. M., 1968, *Foundations of Quantum Mechanics*, Addison-Wesley, Reading, MA, pp. 131-132.
- Jaynes, E. T., 1957, *Physical Review*, Vol. 108, p. 171.
- Korsch, H. J., and Steffen, H., 1987, *Journal of Physics A: Mathematical and General*, Vol. 20, p. 3787.
- Lindblad, G., 1976, *Communications in Mathematical Physics*, Vol. 48, p. 119.
- Meixner, J., 1970, "On the Foundation of Thermodynamics of Processes," *A Critical Review of Thermodynamics*, E. B. Stuart et al., ed., Mono Corp., Baltimore, p. 37 and p. 47.
- Obert, E. F., 1960, *Concepts of Thermodynamics*, McGraw-Hill, New York.
- Ochs, W., 1975, *Reports on Mathematical Physics*, Vol. 8, 1, p. 109.
- Park, J. L., 1968, *American Journal of Physics*, Vol. 36, p. 211.
- Park, J. L., 1988, *Foundations of Physics*, Vol. 18, 2, p. 225.
- Park, J. L., and Simmons, R. F., Jr., 1983, "The Knots of Quantum Thermodynamics," *Old and New Questions of Physics, Cosmology, and Theoretical Biology: Essays in Honor of Wolfgang Yourgrau*, A. van der Merwe, ed., Plenum Press, NY, pp. 289-308.
- Rényi, A., 1966, *Wahrscheinlichkeitsrechnung*, VEB Deutscher Verlag der Wissenschaften, Berlin.
- Schroedinger, E., 1936, *Proceedings of the Cambridge Philosophical Society*, Vol. 32, p. 446.
- Timoshenko, S., and Young, D. H., 1948, *Advanced Dynamics*, McGraw-Hill, p. 1 and p. 106.
- Tisza, L., 1970, in *A Critical Review of Thermodynamics*, E. B. Stuart et al., ed., Mono Book Corp., Baltimore, p. 510.
- Tolman, R. C., 1962, *Principles of Statistical Mechanics*, Oxford University Press, London.
- Tribus, M., 1963, Boelter anniversary volume, McGraw-Hill.
- von Neumann, J., 1929, *Zeitschrift für Physik*, Vol. 57, p. 30.
- von Neumann, J., 1955, *Mathematical Foundations of Quantum Mechanics*, Princeton University Press, Princeton, NJ.
- Wehrl, A., 1978, *Reviews of Modern Physics*, Vol. 50, p. 221.