120

New Developments in Thermodynamics

by

Elias P. Gyftopoulos
Massachusetts Institute of Technology
Cambridge, Massachusetts, USA

Gian Paolo Beretta
Università di Brescia
Brescia, Italy

1. Brief Historical Background

Professor Takehiro Ito read our book on *Thermodynamics: Foundations and Applications* (Macmillan, New York, 1991) and asked us to write a brief article on new developments in thermodynamics. We are very happy to respond.

The word thermo-dynamics was introduced by William Thomson (Lord Kelvin), an Irish-born, British mathematician and physicist, in his papers on "The Dynamical Theory of Heat" [1]. It is derived from the Greek words θερμό (thermó = hot or heat) and δυναμική (dynamiké = time evolution resulting from the application of force; dynamis = force).

The seminal ideas of thermodynamics were introduced by Sadi Carnot, a French military engineer, in his famous pathfinding memoir on the Motive Power of Fire in 1824 [2], and the first and second laws were enunciated by Rudolph Julius Emanuel Clausius, a German mathematical physicist, in a series of papers that appeared from 1851 to 1867 [3]. Correct statements of the second law have also been given by Lord Kelvin [4], Max Ernst Planck [5], a German physicist, and Constantin Caratheodory [6], a Greek mathematician.

Since the beginning, the role of thermodynamics in both science and technology has been continuously broadening. The broadening has come about not because of changes in the basic ideas but because of better understanding of their meaning, range of validity, and universal applicability.

Initially, the broadening of understanding was very much conditioned and restricted by two factors.

The first is the historical association of the origins of the subject with heat, temperature, and equilibrium. This association is so strong and so predominant that even today the vast majority of physicists and engineers define the subject more or less as Guggenheim [7]: "Thermodynamics is that part of physics concerned with the dependence on temperature of any equilibrium property."

This restrictive definition is puzzling in light of the meaning of the term thermodynamics, and its two most important and universally acclaimed conclusions which are demonstrably dynamic — not equilibrium. Specifically, in isolated systems energy is conserved, and entropy does not decrease. These two conclusions would be meaningless and useless unless they refer to time evolution — unless comparisons are made of energies and entropies at different instants of time, always keeping in mind that later results are compared to earlier results and not vice versa.

The second factor is the historical association of entropy with statistics. As is very well known, the science of thermodynamics developed independently of the science of mechanics, and each has been very successful — almost triumphant — in regularizing, with great economy of thought, a large number of phenomena. There is a fundamental problem, however, with these two independent developments.

Both mechanics and thermodynamics deal with systems and their properties, and both recognize energy as a property that has unified our understanding of physical phenomena. According to the theory of mechanics, all the energy of a system is available in principle to affect a mechanical effect. For example, all the energy can be transferred out of a system and used to raise a weight from a low to a high elevation.

On the other hand, according to theory and experience of thermodynamics the situation is different. A system may have a lot of energy and yet not all this energy is available to affect a mechanical effect. Another way of stating this limitation is to say that in thermodynamics a given amount of energy of a system has always associated with it a certain amount of entropy and, if the entropy is large, the ability of the system to do work is less than the energy, and can be even zero.

This fundamental practical and theoretical difference leads to the question "what is entropy?"

Scientists and engineers have been struggling to answer this question for almost a century and a half, and the overwhelming majority feels that a satisfactory answer has been found. The presumed answer can be paraphrased as follows. In reality, matter does not have entropy as a property as it has, for instance, energy and momentum as properties. Entropy is an engineering, nonphysical concept applicable to very large systems only. For such systems, scientists and engineers have neither the tools nor the time to analyze the systems in detail. For this reason, they resort to statistical estimates — introduce subjective probabilities which reflect the ignorance of the professionals — and a measure of the degree of ignorance in each case is entropy.

Perhaps this paraphrasing is somewhat exaggerated, but it is representative of Maxwell-Boltzmann statistics, Gibbsian statistics, and information theory.

Statistical theories of thermodynamics yield many correct and practical results. For example, they yield the canonical and grand canonical distributions. These distributions were proposed by Gibbs [8] and have been shown by innumerable comparisons with experiments to describe accurately the properties of thermodynamic

equilibrium states. Again they predict the equality of temperatures of systems in mutual stable equilibrium, the Maxwell relations, and the Gibbs equation.

Despite these successes, the premise that entropy is a subjective characteristic of the knowledge of a partially informed observer rather than a property of matter and radiation leaves much to be desired in view of many accurate, reproducible, and nonstatistical experiences, such as the mixing of hot and cold, the internal discharge of an insulated battery, and the Peltier effect.

In response to concerns both about the dynamic nature of many thermodynamic phenomena, and a desire to establish entropy as a property of a system rather than an observer, over the past two decades a different conception has been evolving. It is discussed in great detail in our textbook. Here we provide a brief summary only of the foundations.

2. 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 about mechanical dynamics [9]. However, because of the second law, we will see that the definition encompasses a much broader spectrum of phenomena than mechanical dynamics. Said differently, thermodynamics accounts for phenomena with both zero and positive values of entropy, whereas mechanical dynamics of either classical or ordinary quantum mechanics accounts only for phenomena with zero values of entropy.

2.1 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, provided it can be determined by the following specifications.

1. The type of each constituent and the range of values of the corresponding amount.

2. The type and the range of values of the parameters that fully characterize the external forces exerted on the constituents by bodies other than the constituents, such as the parameters that describe an airtight container. The external forces do not depend on coordinates of bodies other than those of the constituents of the system.

3.   The internal forces between constituents, such as intermolecular forces, and forces that account for chemical or nuclear reactions.

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

For a system with r constituents, we denote their amounts by the vector $n = \{n_1, n_2, ..., n_r\}$. For a system with external forces described by s parameters we denote the parameters by the vector $\beta = \{\beta_1, \beta_2, ..., \beta_s\}$. 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 n and β 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.

Two properties are *independent* if the value of one can be varied without affecting the value of the other.

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.

2.2   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.

A system that can experience only spontaneous changes of state is called *isolated*. Systems that are not isolated can interact with each other in a number of different ways, some of which may result in net flows of properties from one system to another. For example, an elastic collision results in the flow or transfer of momentum from one system to the other.

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*. In classical mechanics, the equation of motion is *Newton's equation* which relates the total force F on each system particle to its mass m and acceleration a so that $F = ma$. In quantum mechanics, the equation of motion is the *time-dependent Schroedinger equation*. These equations are incomplete because neither describes either all known reversible time evolutions, or any irreversible time evolution. The discovery of the complete equation of motion remains a subject of research at the frontier of science — one of the most intriguing and challenging problems in physics. Many attempts have been made to establish the equation, but the task requires more work. A notable contribution is described in references [10-12].

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 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.

Rather than through the explicit time dependence which requires the complete equation of motion, a change of state can be described in terms of: (a) the *end states* of the system; (b) the *modes of interaction* that are active during the change of state; and (c) *conditions on the values of properties* of the end states that are consequences of the laws of thermodynamics, that is, conditions that express not all, but the most general and well-established features of the complete equation of motion. Each mode of interaction is characterized by means of well-specified net flows of properties across the boundaries of the interacting systems. For example, after defining the properties energy and entropy, we will see that some modes of interaction involve the flow of energy across the boundaries of the interacting systems without any flow of entropy, whereas other modes of interaction involve the flows of both energy and entropy. Among the conditions on the values of properties, we will see that the energy change of a system must equal the energy transferred to the system, and its entropy change must not be less than the entropy transferred to the system.

The approach just cited is entirely analogous to the approach used in studies of elastic collisions in classical mechanics. In elastic collisions we do not need to solve Newton's equation of motion. We find their effect by conserving kinetic energies and momenta before and after the collision.

2.3 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

$$E_1 = E_0 - Mg(z_1 - z_0)$$

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. It is obtained without use of the general equation of motion.

Energy can be transferred between systems by means of interactions. Denoting by $E^{A\leftarrow}$ the net 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

$$\left(E_2 - E_1\right)_{system\,A} = E^{A\leftarrow}$$

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

The values of energy disclosed by the first law are relative because the choice of the reference value E_0 is arbitrary. The theory of special relativity, however, allows the assignment of absolute energy values in a manner entirely consistent with the first law, and introduces the concept of (inertial) mass.

In general, and in contrast to energy and momentum, mass is neither additive nor conserved. However, in the absence of nuclear reactions, and creation and annihilation reactions, the mass changes caused within a system by energy exchanges between constituents and the electromagnetic field or by chemical reactions are negligible with respect to the mass of the system. As a result, we establish a very useful tool, the *mass balance*, that is

$$\left(m_2 - m_1\right)_{system\ A} = m^{4-}$$

where m^{4-} is the net amount of mass transferred from the environment to system A. The mass m^{4-} is positive when mass is flowing into A.

2.4 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. To facilitate the discussion of these states, we classify them into different categories according to their 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.

An *unsteady state* is one that changes as a function of time because of interactions of the system with other systems. A *steady state* is one that does not change as a function of time despite interactions of the system with other systems in the environment. A *nonequilibrium state* is one that changes spontaneously as a function of time, that is, a state that evolves as time goes on without any effects on or interactions with any other systems. 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.

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.

2.5 Generalized Available Energy

The existence of stable equilibrium states is intimately connected to dynamics but is not self-evident. It was first recognized by George Nicholas Hatsopoulos, a Greek

mechanical engineer, and Joseph Henry Keenan, an American thermodynamicist, in their pioneering textbook *Principles of General Thermodynamics* (Wiley, New York, 1965), as the essence of all correct statements of the second law. We 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 — the ground-state 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. Here, 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 ground-state energy by means of a mechanical effect. This is a generalization of the impossibility of a PMM2.

A third consequence is that the first and second laws impose 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. We call the optimum value *generalized available energy*, and denote it by Ω^R. 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, and we do not use this assumption.

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. In addition, Ω^R is shown to be additive.

2.6   Entropy and Entropy Balance

A system A in any state A_1 has the two properties: energy E_1, and generalized available energy Ω_I^R with respect to a given auxiliary reservoir R. These two properties determine a third one we call *entropy*, and denote by the symbol S_1. It is a property in the same sense that energy is a property, or momentum is a property. It can be evaluated by means of an auxiliary reservoir R, a reference state A_o, with energy E_o and generalized available energy Ω_o^R, to which is assigned a reference value S_o, and the expression

$$S_1 = S_o + \frac{1}{c_R}\left[(E_1 - E_o) - \left(\Omega_I^R - \Omega_o^R\right)\right]$$

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.

The concept of entropy introduced here differs from and is more general than that of most textbooks. It does not involve the concepts of heat and temperature which have not yet been defined; it is not restricted to large systems; it is not restricted to equilibrium states; and most certainly, it is not statistical. To emphasize the difference and generality of the concept, we recall the statements by Meixner [13] "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 [14] "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 entropy 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*. The entropy created as time proceeds during an irreversible process is called *entropy generated by irreversibility*. It is positive. Like energy conservation, entropy nondecrease is a time-dependent result which is obtained without use of the general equation of motion.

Like energy, entropy can be transferred between systems by means of interactions. Denoting by $S^{A\leftarrow}$ the net 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,

$$\left(S_2 - S_1\right)_{system\ A} = S^{A^-} + S_{irr}$$

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 (defined later). The unit of c_R chosen in the International System of units is the kelvin, denoted by K. So entropy can be expressed in J/K or other equivalent units.

2.7   Stable Equilibrium States

An isolated system admits an indefinite number of states that have given values of the energy E, the amounts of constituents $n_1, n_2, ..., n_r$, and the parameters $\beta_1, \beta_2, ..., \beta_s$. Most of these states are nonequilibrium, some are equilibrium, and according to the second law, only one is a stable equilibrium state. It follows that any property of the system in a stable equilibrium state is uniquely determined by the values E, n, β, that is, it can be written as a function of E, n, β only. This result is known as the *stable equilibrium state principle* or simply the *state principle*.

A system in general has a very large number of independent properties. If we focus on the special family of states that are stable equilibrium, however, the state principle asserts that the value of each of these properties is uniquely determined by the values E, n, β or the values of an equivalent set of independent properties. In contrast, for states that are not stable equilibrium, the values of E, n, β are not sufficient to specify the values of all independent properties.

One property of great interest is the entropy of stable equilibrium states. It satisfies the relation

$$S = S(E,\ n,\ \beta)$$

and is called the *fundamental relation*. It is concave in each of the variables $E, n_1, n_2, ..., n_r$, and in each of the parameters $\beta_1, \beta_2, ..., \beta_s$ which are additive, like volume. It is also

concave collectively with respect to all the variables $E, n_1, n_2, ..., n_r$, and the parameters $\beta_1, \beta_2, ..., \beta_s$ which are additive.

The entropy of each unique stable equilibrium state is larger than that of any other state with the same values E, n, β. This result is known as the *highest entropy principle*.

We use the fundamental relation to define the intensive properties

$$T = 1/(\partial S/\partial E)_{n,\beta} = \text{temperature}$$

$$\mu_i = -T(\partial S/\partial n_i)_{E,n,\beta} = \text{total potential of } i\text{th constituent}$$

$$p = T(\partial S/\partial V)_{E,n,\beta} = \text{pressure}$$

$$f_j = -T(\partial S/\partial \beta_j)_{E,n,\beta} = \text{force conjugated to the } j\text{th parameter}$$

where $V = \beta_1$ = volume. These properties are useful because, for mutual stable equilibrium between two systems, the largest entropy principle requires that the temperature, total potentials, pressure, and forces of one system be equal to the corresponding properties of the other system.

Upon solving the fundamental relation for E, we find

$$E = E(S, n, \beta)$$

We can then consider a stable equilibrium state A_0 with energy E_0, entropy S_0, amounts of constituents n_0, and parameters β_0, and any other neighboring stable equilibrium state with energy $E_0 + dE$, entropy $S_0 + dS$, amounts of constituents $(n_i)_0 + dn_i$ for $i = 1, 2, ..., r$, and parameters $(\beta_j)_0 + d\beta_j$ for $j = 1, 2, ..., s$, and express the differentials dS and dE in the forms

$$dS = \left[\left(\frac{\partial S}{\partial E}\right)_{n,\beta}\right]_0 dE + \sum_{i=1}^{r}\left[\left(\frac{\partial S}{\partial n_i}\right)_{E,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial S}{\partial \beta_j}\right)_{E,n,\beta}\right]_0 d\beta_j$$

$$= \frac{1}{T_0} dE - \sum_{i=1}^{r} \frac{(\mu_i)_0}{T_0} dn_i + \frac{p_0}{T_0} dV - \sum_{j=2}^{s} \frac{(f_j)_0}{T_0} d\beta_j$$

11

and

$$dE = \left[\left(\frac{\partial E}{\partial S}\right)_{n,\beta}\right]_0 dS + \sum_{i=1}^{r}\left[\left(\frac{\partial E}{\partial n_i}\right)_{S,n,\beta}\right]_0 dn_i + \sum_{j=1}^{s}\left[\left(\frac{\partial E}{\partial \beta_j}\right)_{S,n,\beta}\right]_0 d\beta_j$$

$$= T_0\, dS - \sum_{i=1}^{r} (\mu_i)_0 dn_i - p_0 dV + \sum_{j=2}^{s} (f_j)_0 d\beta_j$$

These differentials are very useful in studies of properties of substances in stable equilibrium states.

2.8 Work, Heat, and Other Interactions

Interactions can have a great variety of effects. Some result in exchange of energy between the interacting systems while the values of their parameters remain unchanged and neither entropy nor constituents are exchanged. Other interactions result in exchanges of energy and entropy, but neither constituents are exchanged nor the values of the parameters are affected. Still others may result in exchanges of energy, entropy, and constituents, as well as in changes in values of the parameters. Such exchanges result in changing the states of the interacting systems.

In addition, if as a result of interactions a system is brought to a state that is not stable equilibrium, this state may evolve spontaneously toward a stable equilibrium state, thus causing further changes in the values of the properties of the system, including spontaneous generation of entropy.

Knowing how much of the change of a property is due to exchanges with other systems and how much to spontaneous generation or destruction within the system is very important to understanding the performance of the system. For example, if the entropy of a system increases solely because of spontaneous generation — irreversibility — such an increase implies imperfections and is subject to improvement by redesign.

An ingenious method for identifying the system in which entropy is generated by irreversibility is by specifying each interaction in terms of the net exchanges that it causes at the boundary between the interacting systems, and comparing these exchanges to the changes of properties of the system. For this reason we classify interactions into different categories, depending on whether the interacting systems exchange energy and constituents but no entropy, energy and entropy but no constituents, and so on.

Four types of interactions and the corresponding exchanges with respect to one of the interacting systems are listed in Table 1. They are work, heat, bulk flow, and diffusion.

<div align="center">

TABLE 1
EXCHANGES IN FOUR DIFFERENT INTERACTIONS

</div>

EXCHANGE	INTERACTION			
	WORK	HEAT	BULK FLOW[a]	DIFFUSION
ENERGY	W^-	Q^-	$(h+\frac{\xi^2}{2}+gz)n^-$	E^-
ENTROPY	0	$\dfrac{Q^-}{T_Q}$	sn^-	$\dfrac{E^- - \mu_D n^-}{T_D}$
CONSTITUENT	0	0	n^-	n^-

(a) The specific enthalpy h and specific entropy s refer to the stable equilibrium state part of the bulk flow state. The speed ξ, and elevation z in the gravity field g refer to the mechanical features of the bulk flow state. Flow of the constituent is into the system if n^- is positive.

An interaction that results in a net exchange of energy between two systems but no exchange of entropy and constituents is called a *work interaction*. The amount of energy thus transferred to one system is called *work*, and denoted by W^-. Work W^- is positive if energy flows out of the system.

An interaction that results in a net exchange of energy and entropy but no constituents between two systems that are in stable equilibrium states at almost the same temperature T_Q, and such that the ratio of the amount of energy transferred and the amount of entropy transferred is equal to T_Q, is called a *heat interaction*. The energy transferred to one system is called *heat*, and denoted by Q^-. Heat Q^- is positive if energy flows into the system.

The heat definition just cited is necessary because only if it is satisfied heat is entirely distinguishable from work.

An interaction that results in the exchanges listed in the table under bulk flow is called a *bulk flow interaction*. Details about this interaction are given in our textbook, Chapter 22.

Diffusion is another interaction entirely distinguishable from work in that no fraction of it can be regarded as work. It results in net exchanges of energy, entropy, and amount of a constituent between two systems that are in stable equilibrium states at almost the same temperature T_D, and almost the same total potential of the constituent μ_D. For one of the systems, the energy transferred E^-, the amount of constituent transferred n^-, and the entropy transferred S^- are interrelated as listed in the table, and are positive if the flows are out of the system.

Interactions can be combined with the various balances to provide relations between changes of properties of a system and property flows at the boundary of the system. For example, if as a result of heat and work interactions system A changes its state from A_1 to A_2, the energy, entropy and mass balances are

$$\left(E_2 - E_1\right)_{system\ A} = Q^{A-} - W^{A-} = E^{A-}$$

$$\left(S_2 - S_1\right)_{system\ A} = \frac{Q^{A-}}{T_Q} + S_{irr} = S^{A-} + S_{irr}$$

$$\left(m_2 - m_1\right)_{system\ A} = m^{A-} = 0$$

Depending on the type of states A_1 and A_2, changes in properties E, S, m of the system may be expressed in terms of other more convenient properties, and the balances are sufficient to analyze the problem. This is especially true for end states that are stable equilibrium states.

2.9 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 hypersurface 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. Here we discuss the energy versus entropy plane that illustrates many of the basic concepts of thermodynamics. This representation is novel to thermodynamics.

We consider a system with volume V as the only parameter. 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. In our textbook, we prove that the projection must have the shape of the cross-hatched area shown in Figure 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.
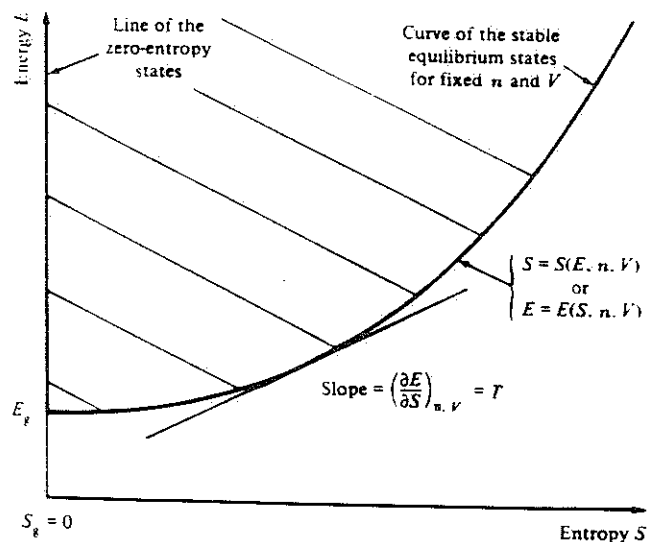
In the figure:
- y-axis: Energy E
- "Line of the zero-entropy states"
- "Curve of the stable equilibrium states for fixed n and V"
- $\begin{cases} S = S(E, n, V) \\ \text{or} \\ E = E(S, n, V) \end{cases}$
- Slope $= \left(\dfrac{\partial E}{\partial S}\right)_{n, V} = T$
- E_g
- $S_g = 0$
- x-axis: Entropy S

Figure 1

A point either inside the cross-hatched area or on the vertical line $S_g = 0$ 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_{S1}, 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_{S1}. This is a graphical illustration of the impossibility of PMM2. It is sometimes expressed as the nonexistence of a *Maxwellian demon*.

Many other results can be depicted on the E versus S graph including generalized available energy, effects of interactions, and effects of irreversibility. They are discussed in our textbook.

3.   How Does Thermodynamics Accommodate Mechanics?

An intriguing question that is raised by the statement of the second law is "how can there be equilibrium and stable equilibrium states — states that involve no motion, zero value of velocity — for any value of the energy?"

This question is especially raised by scientists that are very familiar with the classical kinetic theory of gases in which the only stable equilibrium state is and can be the state of lowest energy.

It belongs to the list of dilemmas and paradoxes that have concerned generations of scientists who during the past century have tried to rationalize the apparent incompatibilities between mechanics and thermodynamics. The rationalization best accepted by the community of physicists is the theory of statistical mechanics, with many successful results such as canonical and grand-canonical, Boltzmann, Bose-Einstein, and Fermi-Dirac distributions. However, the conceptual foundations of this theory, as pointed out by Schroedinger and others [15-17], are shaky and unsound, and seem to require that we abandon the concept of state of a system, a keystone of traditional physical thought. We believe that the weakness of the conceptual foundations has forbidden so far the development of a sound unified theory of nonequilibrium. The

16

situation can be summarized as follows. On one hand, the successes of mechanics, equilibrium thermodynamics, and the formalism of statistical mechanics leave no doubts on the validity of their results. On the other hand, the need remains for a coherent physical theory capable of encompassing these same results within a sound unified conceptual framework.

The notion of stability of equilibrium has played a central role in the efforts to fill the gap. The recognition by Hatsopoulos and Keenan of the central role that stability plays in thermodynamics is in our view one of the most fundamental conceptual advances in physics during the last three decades. It has provided the key to a coherent resolution of the entropy-irreversibility-nonequilibrium dilemma.

The answer to the question raised at the beginning of this section emerges from a recent reformulation of quantum physics [18]. It requires quantum ideas in an essential way. Table 2 summarizes a comparison of the basic concepts and their mathematical representations in classical mechanics and in the new quantum physics that we call general thermodynamics. The list of concepts — system, preparation, property, observable, measurement act, probability of measurement results of observables, value of an observable, state, equation of motion — is common to all paradigms of physics. The paradigms differ in the mathematical representations and interrelations between these concepts.

The major difference between classical mechanics and general thermodynamics is that the probability density of measurement results of observables is a delta function in the phase space of the system in the former, and a self-adjoint, nonnegative definite, unit-trace, linear operator ρ on the Hilbert space $\mathcal{H}$ of the system in the latter. This operator satisfies the relations

$$\rho^\dagger = \rho; \quad \rho \geq 0; \quad \mathrm{Tr}\rho = 1; \quad \rho^2 = \rho$$

for the restricted class of states of conventional quantum mechanics, and

$$\rho^\dagger = \rho; \quad \rho \geq 0; \quad \mathrm{Tr}\rho = 1; \quad \rho^2 \neq \rho$$

for the additional broader class of states of general thermodynamics, where $\rho^\dagger$ denotes the adjoint operator of ρ.

The removal of the condition of idempotence ($\rho^2 = \rho$) of the operator ρ implies the conclusion [18] that the state domain of a physical system is larger than that of quantum mechanics. If the operator is idempotent, that is, $\rho^2 = \rho$, then ρ is a one-dimensional projector onto the linear span of some vector ψ in the Hilbert space $\mathcal{H}$, i.e., $\rho = P_\psi$, and corresponds to a *mechanical state*, that is, a state of conventional quantum mechanics. If ρ is not idempotent then it corresponds to a *nonmechanical state*, that is, a state not contemplated by conventional quantum mechanics.

TABLE 2

CONCEPT	VERBAL AND MATHEMATICAL DESCRIPTIONS	
	CLASSICAL MECHANICS	GENERAL THERMODYNAMICS
SYSTEM	CONSTITUENTS (TYPES AND AMOUNTS) IN A NEST OF INTERNAL AND EXTERNAL FORCES	
	REGION IN PHASE SPACE Ω	HILBERT SPACE $\mathcal{H}$, AND SET $\mathfrak{U}(\mathcal{H})$ OF SELF-ADJOINT OPERATORS ON $\mathcal{H}$
KINEMATICS	SNAPSHOT AT ANY ONE INSTANT OF TIME	
PREPARATION	REPRODUCIBLE SCHEME TO GENERATE HOMOGENEOUS ENSEMBLE OF SYSTEMS FOR STUDY	
PROPERTY	SYSTEM ATTRIBUTE . IT CAN BE QUANTITATIVELY EVALUATED AT ANY INSTANT OF TIME BY MEANS OF MEASUREMENTS . RESULT DOES NOT DEPEND ON EITHER OTHER SYSTEMS OR OTHER TIMES .	
OBSERVABLE	SPECIALLY DEFINED PROPERTY	
	FUNCTION $f(q,p)$ on Ω	LINEAR FUNCTIONAL ON $\mathfrak{U}(\mathcal{H})$ $a(\bullet) = \text{Tr}(A\bullet)$ $A =$ HERMITIAN OPERATOR
MEASUREMENT ACT	REPRODUCIBLE SCHEME OF MEASUREMENTS AND OPERATIONS ON A MEMBER OF A HOMOGENEOUS ENSEMBLE . RESULT IS A PRECISE NUMBER WHICH IS ASSOCIATED WITH A DEFINITE OBSERVABLE .	
PROBABILITY DENSITY OF MEASUREMENT RESULTS OF OBSERVABLES	FREQUENCY OF RESULTS OF MEASUREMENT ACTS ON A HOMOGENEOUS ENSEMBLE	
	POINT IN Ω: $\rho = \delta(q - q_0)\,\delta(p - p_0)$	OPERATOR ρ ON $\mathfrak{U}(\mathcal{H})$: $\rho \geq 0; \quad \text{Tr}\rho = 1; \quad \rho^2 = \rho \text{ or } \rho^2 \neq \rho$
VALUE OF AN OBSERVABLE	ARITHMETIC AVERAGE OF MEASUREMENT RESULTS OF THE OBSERVABLE PERFORMED ON A HOMOGENEOUS ENSEMBLE	
	$f(q_0, p_0) = \int \rho f dq dp$	$a(\rho) = \text{Tr}A\rho$
STATE	INSTANTANEOUS VALUES SPECIFYING SYSTEM AND A SET OF INDEPENDENT PROPERTIES	
DYNAMICS	CAUSAL EVOLUTION OF PROPERTIES WITH TIME	
EQUATION OF MOTION OF A SYSTEM	$\dot{q}_i = \{q_i, H\}$ $\dot{p}_i = -\{p_i, H\}$ $H =$ HAMILTONIAN FUNCTION $\{ , \} =$ POISSON BRACKET	REMAINS TO BE ESTABLISHED . CRITERIA: THE TWO LAWS OF THERMODYNAMICS . FOR ATTEMPTS SEE REFERENCES [10 - 12] . IF $\rho^2 = \rho$, IT MUST REDUCE TO THE FORM $\dot{\rho} = i[\rho H - H\rho]/h$ $H =$ HAMILTONIAN OPERATOR

In this way, the entire body of results of quantum mechanics, so successful in describing empirical data, is retained as a whole. In addition, the successful part of the mathematical formalism of statistical mechanics that relates to equilibrium thermodynamics is also included. But the rest of statistical mechanics, that is, its troublesome statistical interpretation, is removed from the theory. In other words, the new theory retains only the successful mathematics but not the unsound interpretation and conceptual foundations of statistical mechanics.

Of course, one of the most revolutionary ideas introduced by quantum mechanics has been the existence, within the individual state of any system, of an indeterminacy resulting in irreducible dispersions of measurement results. This indeterminacy (usually expressed as the Heisenberg uncertainty principle) is embedded in the mathematical structure of quantum mechanics and is fully contained in the description of states by means of vectors ψ in a Hilbert space. The indeterminacy is not removed by the augmentation of the state domain. Rather, a second level of indeterminacy is added for states that are not mechanical, that is, states such that $\rho^2 \neq \rho$. This second measure is the entropy, represented by the functional $-k\mathrm{Tr}\rho\ln\rho$. It is exactly as fundamental and irreducible as the Heisenberg indeterminacy.

The richness of the new augmented kinematics guarantees enough room for the resolution of the many questions that must be addressed in order to complete the theory and accomplish the necessary unification. Among these questions, the first is whether the second law of thermodynamics can be part of the new theory without having to resort to statistical, phenomenological or information-theoretic arguments. The answer is yes. The second law is a statement of existence and uniqueness of a stable equilibrium state for each set of values of the energy functional, the number-of-particle functionals and the parameters. Adjoining this statement to the structure of the new kinematics leads to the identification of the state operators that represent stable equilibrium states, and to the proof that only the functional $-k\mathrm{Tr}\rho\ln\rho$ can represent the thermodynamic entropy. Mathematically, the states of equilibrium thermodynamics are represented by exactly the same operators as in statistical mechanics.

A second intriguing question is "how do all the states ($\rho^2 \neq \rho$) evolve in time?" Such states are beyond the realm of quantum mechanics and, therefore, we cannot expect to derive their time evolution from the equation of motion of mechanics. We have to find a new, complete dynamical law for these states.

In view of the breadth of the set of states in the augmented kinematics, the problem might seem extremely open to a variety of different approaches. A careful analysis, however, shows that the problem is very much constrained by a number of restrictions imposed by the many conditions that such a general dynamical law must satisfy [10-11]. A dynamical law that satisfies all the known conditions is presented in References [10] and [11]. Evidence that the proposed law is the only one that satisfies all these conditions is given in Reference [19].

18

4. Concluding Remarks

During the past twenty years of teaching thermodynamics to students from all over the globe, we have sensed a need for more clarity, unambiguity and logical consistency in the exposition of thermodynamics than provided by traditional approaches. Continuing the effort pioneered by Keenan and Hatsopoulos, in our textbook *Thermodynamics: Foundations and Applications* we have composed an exposition in which we strive to develop the basic concepts without ambiguities and logical inconsistencies, building upon the student's sophomore background in introductory physics.

The basic concepts and principles are introduced in a novel sequence that eliminates the problem of incomplete definitions, and that is valid for both macroscopic and microscopic systems, and for both equilibrium and nonequilibrium states. The laws of thermodynamics are presented as fundamental laws of physics that complement the laws of dynamics. Thus, we emphasize the original conception of thermo-dynamics.

Among many other important clarifications that emerge from our revisitation of the subject, one concerns the removal of the logical circularity that is inherent in ordinary definitions of heat, and that permeates the entire subsequent exposition of the principles of thermodynamics. Such definitions have been adopted in all treatises and textbooks on the subject, both for physics and engineering students. For example, Landau and Lifshitz [20] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim [21] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [22] defines heat as that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. Similar definitions are adopted in notable recent and successful textbooks, such as Van Wylen and Sonntag [23], Wark [24], Huang [25], Modell and Reid [26], and Moran and Shapiro [27].

Invariably, concepts of mechanics are used to justify and make plausible the concept of heat, even though the concept is beyond the realm of mechanics. For example, in his lectures on physics, Feynman [28] describes heat as one of several different forms of energy related to the jiggling motion of particles stuck together and tagging along with each other, a form of energy which really is just kinetic energy — internal motion — and is measured by the random motions of the atoms. Tisza [29] argues that such slogans as "heat is motion," in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value.

The trick works at first, because students have only mechanical ideas in their backgrounds, and so find these mechanistic slogans about heat harmless, even natural.

But the situation changes drastically as soon as the notion of heat is used to define a host of new ideas, less natural and less harmless. At once, heat is raised to the same dignity as work, it is contrasted to work and used as an essential ingredient in the first law, and later as the main ingredient to define entropy. Only at the end it is admitted that entropy cannot be understood by simply using mechanical concepts. But then the

student is lost: How can this be, if entropy has been defined in terms of heat, and heat in terms of mechanical concepts?

In our view, this circularity in the logical presentation has been very harmful to the development of thermodynamics, and to the understanding of its dynamic character. It has been assimilated so deeply by so many practitioners, that some believe that circular arguments are essential ingredients of any theory! As a result, whenever heat is introduced before the first law, and then used in the statement of the second law and in the definition of entropy, the student cannot avoid but sense ambiguity and lack of logical consistency. This results in the wrong but unfortunately widely spread conviction that thermodynamics is a confusing, ambiguous, hand-waving subject.

We feel strongly that this wrong conviction must be and can be dismantled. As already pointed out by Hatsopoulos and Keenan [30], without the second law heat and work would be indistinguishable and, therefore, a satisfactory definition of heat is unlikely without a prior statement of the second law.

The sequence of exposition in our textbook has been developed precisely to emphasize the dynamic character of thermodynamics, and to avoid any circularity in the logic of presentation. In our experience, these features are necessary and sufficient to strengthen the student's confidence in the subject.

Heat plays no role in the first law, the definition of energy, the second law, the definition of entropy, and the concepts of energy and entropy exchanges between interacting systems. It emerges as a consequence of these concepts and laws. How this is done is an important novel development in thermodynamics. It is described in our textbook.

In this article, we summarize and illustrate some key aspects of the novel logical sequence that we propose. The exposition in our book makes no reference to the ideas and mathematics of quantum theory, because the book is intended primarily for engineers. Nevertheless, the exposition is construed so as to be entirely compatible with quantum theory, especially as it concerns the analytical expression of entropy for nonequilibrium states.

The tie with quantum ideas is the most interesting novel development of thermodynamics because it brings forth the need to understand the general principles governing the dynamics of nonequilibrium states, that is, the problem of establishing a complete equation of motion capable of describing in all details the natural tendency of the internal dynamics of all systems towards stable equilibrium. An important step in this direction has been taken.

20

References

1. W. Thomson, "On the Dynamical Theory of Heat, With Numerical Results Deduced from Mr. Joule's Equivalent of a Thermal Unit, and M. Regnault's Observations on Steam," *Mathematical and Physical Papers of William Thomson*, Vol. 1, Cambridge University Press, 1882, pp. 174-200.

2. S. Carnot, *Reflections on the Motive Power of Fire*, Dover Publications, New York, 1960.

3. R. Clausius, "On the Application of the Theorem of the Equivalence of Transformations to the Internal Work of a Mass of Matter," *Philos. Mag.*, ser. 4, 24(159,160), 1862, pp. 81-97, 201-213; and "Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der Mechanischen Wärmetheorie," *Abhandlungen über die mechanische Wärmetheorie*, Vol. II, Vieweg, Braunschweig, 1867, pp. 1-44.

4. W. Thomson, loc. cit., p. 179.

5. M. Planck, *Treatise on Thermodynamics*, Dover Publications, New York, 1945.

6. C. Caratheodory, "Untersuchungen über die Grundlagen des Thermodynamik," *Math. Ann.*, 67, 1909, pp. 355-386.

7. E. A. Guggenheim, *Thermodynamics*, Fifth Revised Edition, North-Holland, 1967, p. V.

8. J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, Dover Publications, New York, 1960.

9. S. Timoshenko and D. H. Young, *Advanced Dynamics*, McGraw-Hill, New York, 1948, p. 1 and p. 106.

10. G. P. Beretta, E. P. Gyftopoulos, J. L. Park, and G. N. Hatsopoulos, "Quantum Thermodynamics. A New Equation of Motion for a Single Constituent of Matter," *Il Nuovo Cimento*, Vol. 82B, 1984, pp. 169-191.

11. G. P. Beretta, E. P. Gyftopoulos, and J. L. Park, "Quantum Thermodynamics. A New Equation of Motion for a General Quantum System," *Il Nuovo Cimento*, Vol. 87B, 1985, pp. 77-97.

12. G. P. Beretta, "Quantum Thermodynamics of Nonequilibrium. Onsager Reciprocity and Dispersion-Dissipation Relations," *Foundations of Physics*, Vol. 17, 4, 1987, pp. 365-381.

13. J. Meixner, "On the Foundation of Thermodynamics of Processes," in *A Critical Review of Thermodynamics*, E. B. Stuart, B. Gal-Or, and A. J. Brainard, editors, Mono Corp., Baltimore, 1970, p. 37 and p. 47.

14. H. B. Callen, *Thermodynamics and Introduction to Thermostatics*, Second Edition, Wiley, New York, 1985, p. 27.

15. E. Schrödinger, *Proceedings of the Cambridge Philosophical Society*, Vol. 32, 446 (1936).

16. J. L. Park, *American Journal of Physics*, Vol. 36, 211 (1968).

17. J. L. Park, *Foundations of Physics*, Vol. 18, 225 (1988).

18. G. N. Hatsopoulos and E. P. Gyftopoulos, "A Unified Quantum Theory of Mechanics and Thermodynamics. Part I. Postulates," *Foundations of Physics*, 6, 1, 1976, pp. 15-31; "A Unified Quantum Theory of Mechanics and Thermodynamics. Part IIa. Available Energy," *Foundations of Physics*, 6, 2, 1976, pp. 127-141; "A Unified Quantum Theory of Mechanics and Thermodynamics. Part IIb. Stable Equilibrium States," *Foundations of Physics*, 6, 4, 1976, pp. 439-455; "A Unified Quantum Theory of Mechanics and Thermodynamics. Part III. Irreducible Quantal Dispersions," *Foundations of Physics*, 6, 5, 1976, pp. 561-570.

19. H. J. Korsch and H. Steffen, *Journal of Physics A*, Vol. 20, 3787 (1987).

20. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part I, 3rd Ed., Revised by E. M. Lifshitz and L. P. Pitaevskii, Translated by J. B. Sykes and M. J. Kearsley, Pergamon Press, 1980, p. 45.

21. E. A. Guggenheim, *Thermodynamics*, Fifth Revised Edition, North-Holland, 1967, p. 10.

22. J. H. Keenan, *Thermodynamics*, Wiley, New York, 1941, p. 6.

23. G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, 2nd Edition, Wiley, New York, 1978, p. 76.

24. K. Wark, *Thermodynamics*, 4th Edition, McGraw-Hill, New York, 1983, p. 43.

25. F. F. Huang, *Engineering Thermodynamics*, Macmillan, New York, 1976, p. 47.

26. M. Modell and R. C. Reid, *Thermodynamics and Its Applications*, Prentice-Hall, Englewood Cliffs, New Jersey, 1983, p. 29.

27. M. J. Moran and H. N. Shapiro, *Fundamentals of Engineering Thermodynamics*, Wiley, New York, 1988, p. 46.

28. R. Feynman, *Lectures on Physics*, Vol. 1, Addison-Wesley, 1963.

29. L. Tisza, *Generalized Thermodynamics*, MIT Press, 1966, p. 16.

30. G. N. Hatsopoulos and J. H. Keenan, *Principles of General Thermodynamics*, Wiley, New York, 1965, p. xxiii.