

# A Novel Sequence of Exposition of Engineering Thermodynamics\*

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*We present the foundations of thermodynamics in a novel sequence in which all basic concepts are defined in terms of well known mechanical ideas. Many definitions are new. The order of introduction of concepts is: system (constituents and parameters); properties; state; energy (without heat and work) and energy balance; classification of states in terms of time evolution; existence of stable equilibrium states; available energy; entropy (without heat and temperature) of any state (equilibrium or not) and entropy balance; properties of stable equilibrium states; temperature in terms of energy and entropy; chemical potentials; pressure; work; heat; applications of balances. This novel sequence not only generalizes the subject of thermodynamics to all systems (large or small) and all states (equilibrium and not equilibrium) but also avoids both the conceptual and definitional difficulties that have been recognized by so many teachers, and the confusion experienced by so many students. [DOI: 10.1115/1.4026385]*

## Introduction

In many expositions of thermodynamics, the concept of heat is introduced at the outset of the logical development in terms of mechanical illustrations aimed at demonstrating the difference between heat and work.

For example, in his lectures on physics, Feynman [1] 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 (pp. 1–3 and 4–2), a form of energy which really is just kinetic energy — internal motion (p. 4–6), and is measured by the random motions of the atoms (p. 10–S). Tisza [2] argues that such slogans as “heat is motion,” in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value.

There are at least two problems with these illustrations. First, work and heat are not stored in a system. Each is a mode of transfer of energy from one system to another. Second, and perhaps more important, concepts of mechanics are used to justify and make plausible a notion — that of heat — which is beyond the realm of mechanics. In spite of these logical drawbacks, the trick works because at first the student finds the idea of 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. The student begins to worry because the notion of heat is less definite than and not as operational as that of work.

The first problem is addressed in some expositions. Landau and Lifshitz [3] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim [4] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [5] 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 textbooks, such as Van Wylan and Sonntag [6], Wark [7], Huang [8], Modell and Reid [9], and Moran and Shapiro [10].

None of these definitions, however, addresses the basic problem. The existence of exchanges of energy that differ from work is not granted by mechanics. It is one of the striking results of thermodynamics, that is, of the existence of entropy as a property of matter. Hatsopoulos and Keenan [11] have pointed out explicitly that without the second law heat and work would be indistin-

guishable and, therefore, a satisfactory definition of heat is unlikely without a prior statement of the second law.

In our experience, 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.

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, we have composed an exposition [12] 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. 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. Heat is the energy exchanged between systems that interact under very restrictive conditions that define what we call a heat interaction.

In this presentation we summarize the key aspects of the novel logical sequence that we propose in our exposition of the foundations of thermodynamics. It is an abbreviated version of Chapter 14 of our book [12]. Although it makes no reference to the ideas of quantum thermodynamics, the exposition is construed so as to be entirely compatible with quantum physics because such compatibility is absolutely essential to the definition of entropy for nonequilibrium states and its existence as a property of matter.

Many simple numerical and graphical illustrative examples are presented in Chapters 2 to 13 of Reference 12. In the interest of brevity we do not repeat them here.

We cover the material discussed in this paper in the first 10 one-hour lectures of our undergraduate course in engineering thermodynamics.

## Lecture 1

**General Thermodynamics.** We define general thermodynamics or simply thermodynamics as the study of motions of physical

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

**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. The internal forces depend on the coordinates of all the interacting constituents.

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

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

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.

## Lecture 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*. 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.

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.

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, that is, the initial and final states; (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.

The end states and the modes of interaction that are active during the change of state define a *process*.

## Lecture 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. 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

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

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

$$(m_2 - m_1)_{\text{system } A} = m^{A-}$$

where  $m^{A-}$  is the net amount of mass transferred from the environment to system  $A$ . The mass  $m^{A-}$  is positive if mass flows into  $A$ .

## Lecture 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.

## Lectures 5 and 6

**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 [14] 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. 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 just 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 state of lowest energy by means of a mechanical effect. This is a generalization of the impossibility of a PMM2. In essence, we prove the existence of a novel important property that we call *adiabatic availability* and denote by  $\Psi$ . The 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 adiabatic availability, we 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, we 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. We call the optimum value *generalized available energy*, and denote it by  $\Omega^R$ . 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,  $\Omega^R$  is shown to be additive.

## Lecture 7

**Entropy and Entropy Balance.** A system  $A$  in any state  $A_1$  has the two properties: energy  $E_1$ , and generalized available energy  $\Omega_1^R$  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  $\Omega_o^R$ , to which is assigned a reference value  $S_o$ , and the expression

$$S_1 = S_o + \frac{1}{c_R} [(E_1 - E_o) - (\Omega_1^R - \Omega_o^R)]$$

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 applies to macroscopic as well as microscopic systems, including a system with one particle with only one (translational) degree of freedom; it is not restricted to equilibrium states; it is defined for both equilibrium and not equilibrium states because energy and generalized available energy are defined for all states; and most certainly, it is not statistical. To emphasize the difference and generality of the concept, we recall contrary statements by Meixner [15] "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 [16] "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, we prove 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*. 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. 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  $S^{A-}$  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,

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

where  $S_{\text{irr}}$  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.

## Lecture 8

**Stable Equilibrium States.** An isolated system admits an indefinite number of states that have given values of the energy  $E$ , the amounts of constituents  $n_1, n_2, \dots, n_r$ , and the parameters  $\beta_1, \beta_2, \dots, \beta_s$ . 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  $E, n, \beta$ , that is, it can be written as a function of  $E, n, \beta$  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  $E, n, \beta$  or the values of an equivalent set of independent properties. In contrast, for states that are not stable equilibrium, the values of  $E, n, \beta$ , 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  $E, n_1, n_2, \dots, n_r$ , and in each of the parameters  $\beta_1, \beta_2, \dots, \beta_s$  which are additive, like volume.

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

We use the fundamental relation to introduce some intensive properties that are defined for stable equilibrium states only. They are

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

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

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

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

where  $V = \beta_V = \text{volume}$ . 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. Two systems are in mutual stable equilibrium if their composite is in a stable equilibrium state.

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  $\beta_0$  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  $i=1,2,\dots,r$ , and parameters  $(\beta_j)_0 + d\beta_j$  for  $j=1,2,\dots,s$ , and express the differentials  $dS$  and  $dE$  in the forms

$$\begin{aligned}
dS &= \left[ \left( \frac{\partial S}{\partial E} \right)_{n,\beta} \right]_0 dE + \sum_{i=1}^r \left[ \left( \frac{\partial S}{\partial n_i} \right)_{E,n,\beta} \right]_0 dn_i \\
&+ \sum_{j=1}^s \left[ \left( \frac{\partial S}{\partial \beta_j} \right)_{E,n,\beta} \right]_0 d\beta_j \\
&= \frac{1}{T_0} dE - \sum_{i=1}^r \frac{(\mu_i)_0}{T_0} dn_i + \frac{p_0}{T_0} dV - \sum_{j=2}^s \frac{(f_j)_0}{T_0} d\beta_j
\end{aligned}$$

and

$$\begin{aligned}
dE &= \left[ \left( \frac{\partial E}{\partial S} \right)_{n,\beta} \right]_0 dS + \sum_{i=1}^r \left[ \left( \frac{\partial E}{\partial n_i} \right)_{S,n,\beta} \right]_0 dn_i \\
&+ \sum_{j=1}^s \left[ \left( \frac{\partial E}{\partial \beta_j} \right)_{S,n,\beta} \right]_0 d\beta_j \\
&= T_0 dS + \sum_{i=1}^r (\mu_i)_0 dn_i - p_0 dV + \sum_{j=2}^s (f_j)_0 d\beta_j
\end{aligned}$$

where in writing the second forms of  $dS$  and  $dE$  we use the definitions of  $T$ ,  $\mu_i$ ,  $p$ , and  $f_j$ . These differentials are very useful in studies of properties of substances in stable equilibrium states.

## Lecture 9

**Work and Heat Interactions.** At this stage, we are ready to introduce the definitions of some 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, or energy and entropy but no constituents, and so on.

Two types of interactions are work and heat.

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 between the two systems is called *heat*, and denoted by  $Q^-$ . Heat  $Q^-$  is positive if energy flows into the system. The definition is also valid if one of the two interacting systems passes through stable equilibrium states at temperature  $T_Q$ , and the energy and entropy exchanged are  $Q^-$  and  $Q^-/T_Q$  respectively.

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

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

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

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

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

It is noteworthy that here the energy balance is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called “the first law.” Similarly, the entropy balance is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called “the second law.”

Work and heat are ingenious concepts. For given end states of a system, they allow the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions with other systems. As such, these two concepts provide practical means for identifying opportunities to reduce the entropy generation by irreversibility and, hence, improve the performance of the system. The identification of these opportunities would be missed if heat were defined as just any interaction that is not work, i.e., any nonwork interaction.

## Lecture 10

**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. 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. The laws of thermodynamics imply 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.

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

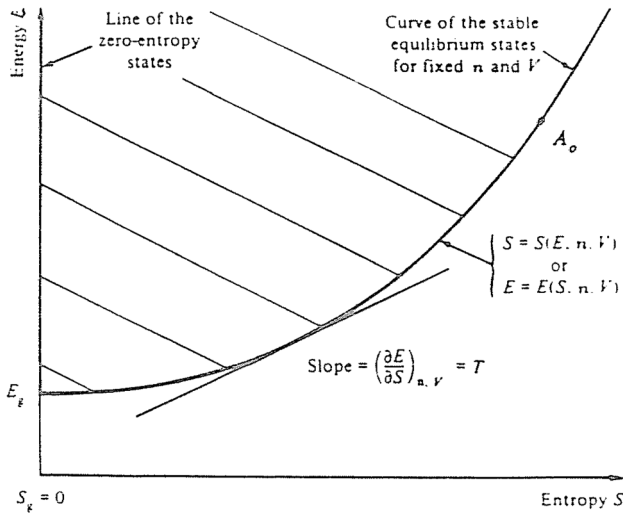


Fig. 1

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  $A_{ST}$ , 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  $A_{ST}$ . This is a graphical illustration of the impossibility of PMM2. It is sometimes expressed as the non-existence of a *Maxwellian demon*.

## Conclusions

In our experience with undergraduate teaching in an engineering school, we manage to develop the preceding sequence in the first 10 hours of the course. After these lectures, we proceed with applications of energy and entropy balances to heat engines, simple systems, Euler and Maxwell relations, the phase rule, two-phase states, bulk-flow interactions, energy conversion devices, and other standard applications.

We find that exposing the undergraduate students to all the precise definitions and also to some of the key proofs, instead of just saying “it can be proved” on all occasions, has two advantages: first, the students gain a precise idea of the nature of the logic involved in physics, and the explicit role of the two laws of thermodynamics; and second, the students build up much more confidence in all the results if they have seen, at least for some of them, the precise and rigorous logic that is behind. This is exactly what we believe is missing in traditional expositions. And it is what traditional expositions cannot give because the teacher must cover up for the usual logical faults and circularities.

In conclusion, the strength of the new approach is that the soundness of the body of definitions and the complete rigor of the logical development, even if not presented in its full glory to the undergraduate, nevertheless lurks behind the whole exposition, leaving no space for doubts on the general validity of the results.

## References

- [1] Feynman, R., *Lectures on Physics*, Vol. 1, Addison-Wesley, 1963.
- [2] Tisza, L., *Generalized Thermodynamics*, MIT Press, 1966, p. 16.
- [3] Landau, L. D. and Lifshitz, E. M., *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.
- [4] Guggenheim, E. A., *Thermodynamics*, 7th Ed., North-Holland, 1967, p. 10.
- [5] Keenan, J. H., *Thermodynamics*, Wiley, 1941, p. 6.
- [6] Van Wylen, G. J., and Sonntag, R. E., *Fundamentals of Classical Thermodynamics*, 2nd Ed., Wiley, 1978, p. 76.
- [7] Wark, K., *Thermodynamics*, 4th Edition, McGraw-Hill, 1983, p. 43.
- [8] Huang, F. F., *Engineering Thermodynamics*, Macmillan, 1976, p. 47.
- [9] Modell, M., and Reid, R. C., *Thermodynamics and Its Applications*, Prentice-Hall, 1983, p. 29.
- [10] Moran, M. J., and H. N., Shapiro, *Fundamentals of Engineering Thermodynamics*, Wiley, 1988, p. 46.
- [11] Hatsopoulos, G. N., and J. H. Keenan, *Principles of General Thermodynamics*, Wiley, 1965, p. xxiii.
- [12] Gyftopoulos, E. P., and Beretia, G. P., *Thermodynamics. Foundations and Applications*, Macmillan, 1991.
- [13] Timoshenko, S., and Young, D. H., *Advanced Dynamics*, McGraw-Hill, 1948, p. 1 and p. 106.
- [14] Hatsopoulos, G. N., and Keenan, J. H., *Principles of General Thermodynamics*, Wiley, 1965, p. 367.
- [15] Meixner, J., “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.
- [16] Callen, H. B., *Thermodynamics and Introduction to Thermostatistics*, Second Edition, Wiley, 1985, p. 27.