

PRESENTATION OF THE FOUNDATIONS OF THERMODYNAMICS IN ABOUT TWELVE ONE-HOUR LECTURES

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1. Introduction

In many expositions of thermodynamics, heat is introduced at the outset of the logical development as an intuitive and self-evident concept, independent of the laws of the subject [1, 2].

For example, Feynman [3] 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 [3, pp. 1–3 and 4–2], a form of energy which really is just kinetic energy — internal motion [3, p. 4–6], and is measured by the random motions of the atoms [3, p. 10–8]. Tisza [4] argues that such slogans as “heat is motion,” in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value. Brush [5] entitles his two-volume history of the kinetic theory of gases “The kind of motion we call heat.”

There are at least two problems with these illustrations. First, work and heat are not stored in a system. Second, and perhaps more important, concepts of mechanics are used to justify and make plausible the notion 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 heat is used to define a host of new concepts, less natural and less harmless. Heat is contrasted to work and used as an essential ingredient in the first law. The student begins to worry because heat is less definite than and not as operational as work.

An attempt to address the first problem is made in some expositions. Landau and Lifshitz [6] define heat as the part of an energy change of a body that is not due to work. Guggenheim [7] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [8] defines heat as that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, if the two are brought into communication. Similar definitions are adopted in other textbooks.

These definitions, however, are ambiguous, and none addresses the basic problem, that is, the existence of exchanges of energy that differ from work, and cannot be justified by mechanics. Such exchanges are one of the striking results of thermodynamics, and are due to entropy being a property of matter. Hatsopoulos and Keenan [9] have pointed out explicitly that 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.

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, and hand-waving subject.

During the past three decades of teaching thermodynamics to students from all over the globe, we have sensed a need to address these concerns. In response, we have composed an exposition [10] 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 stable or thermodynamic equilibrium states and for states that are not stable equilibrium. The laws of thermodynamics are presented as partial complements to the incomplete law of mechanical dynamics. Heat plays no role in the first law, the definition of energy, the second law, the definition of entropy, and the general concepts of energy and entropy exchanges between interacting systems. It emerges as a consequence of these concepts and laws. The discussion that follows is a summary of the key aspects of the novel logical sequence that we propose in our exposition. Though it makes no reference to the ideas of quantum thermodynamics, the exposition is construed so as to be entirely compatible with quantum theory. Such compatibility is absolutely essential to the resolution of the dilemma about the relation between mechanics and thermodynamics.

Experience at the University of Brescia, Italy, and MIT, Tufts University, Northeastern University, Washington University in St. Louis, and the University of Florida in the USA indicates that the fundamental ideas can be presented in about twelve one-hour lectures, with sufficient time for explanations and illustrations short of elaborate proofs. In what follows, we provide a syllabus of the twelve lectures without the necessary numerical and graphical illustrative examples given in [10]. However, the use of numerical and graphical illustrations is absolutely necessary and strongly recommended.

A variant of the sequence of the topics is to begin with the energy versus entropy graphs of Lecture 11 without defining any term. This approach gives the students a visual conception of the ideas that are presented in Lectures 1 to 10, and stimulates interest in the details of the course.

2. Lecture 1

2.1. 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 [11]. 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 classical mechanics and ordinary quantum mechanics account only for phenomena with zero values of entropy.

2.2. KINEMATICS: CONDITIONS AT AN INSTANT IN TIME

In kinematics we give verbal definitions of the terms system, environment, 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.

2.2.1. *System*

A *system* is defined as a collection of constituents. For our purposes, we consider only one constituent which is determined by the following specifications: (a) The type of the constituent and the range of values of its amount; (b) The type and the range of values of the parameters that fully characterize the external forces exerted on the constituent by bodies other than the constituent itself, such as the volume of a container. The external forces do not depend on coordinates of bodies other than those of the constituent of the system. For our purposes, we consider only volume as a parameter; and (c) The internal forces between particles of the constituent, such as intermolecular forces. The internal forces depend on the coordinates of all the interacting particles.

Everything that is not included in the system is the *environment*. We denote the amount of the constituent by n , and the value of the volume by V . At any instant in time, the amount of the constituent and the volume have specific values. We denote these values by n and V with or without additional subscripts.

2.2.2. *Property*

By themselves, the values of the amount of the constituent and of the volume at an instant in time do not suffice to characterize completely the condition of the system at that time. We also need the values of properties at the same instant in time. A *property* is an attribute that can be evaluated at any given instant in 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 in time.

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

2.2.3. *State*

For a given system, the values of the amount of the constituent, the value of the volume, and the values of a complete set of independent properties encompass all that can be said about the system at an instant in time and about the results of any measurements that may be performed on the system at that same instant. We call this complete characterization of the system at an instant in time the *state* of the system. Without change, this definition of state applies to any branch of physics.

3. Lecture 2

3.1. DYNAMICS: CHANGES OF STATE IN TIME

3.1.1. *Equation of Motion*

The state of a system may change in time either spontaneously as the constituent tries to conform to the external and internal forces or as a result of interactions with other systems, or both. A system that experiences only spontaneous changes of state is called *isolated*. A system that is not isolated interacts with the environment in a number of different ways, some of which may result in net flows of properties between the system and the environment. For example, collision between a system and the environment results in the flow or transfer of momentum to or from the system.

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 inertial 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 thermodynamics.

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 presented in subsequent lectures.

3.1.2. *Interactions and Processes*

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 *interactions* that are active during the change of state; (b) the *end states* of the system, that is, the initial and final states; 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 interaction is characterized by means of well-specified net flows of properties across the boundary of the system. For example, after defining the properties energy and entropy, we will see that some interactions involve the flow of energy across the boundary of the system without any flow of entropy, whereas other interactions 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 exchanged between the system and its environment, whereas the entropy change must not be less than the entropy exchanged between the system and its environment.

4. Lecture 3

4.1. 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 but is not a part of the statement of that law.

4.2. 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 inertial mass of the weight, and g the gravitational acceleration.

4.2.1. Definition of Energy

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

$$E_1 = E_0 - Mg(z_1 - z_0) \quad (1)$$

Energy is an *additive property*, that is, the energy of a composite system is the sum of the energies of its subsystems. Moreover, energy either has the same value at the final time as at the initial time if the process is a zero-net-effect weight process, or remains invariant in time if the process is spontaneous. In either of these 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. It is noteworthy that energy is defined for any system (both macroscopic and microscopic) and for any state, and is not statistical.

4.2.2. Energy Balance

In the course of interactions, energy can be exchanged between a system and its environment. Denoting by $E^{A\leftarrow}$ the amount of energy exchanged between the environment and 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

$$(E_2 - E_1)_{\text{system } A} = E^{A\leftarrow} \quad (2)$$

where $E^{A\leftarrow}$ is positive if energy flows into A . In words, the energy change of system A must be accounted for by the net energy crossing the boundary of the system.

4.3. MASS BALANCE

The values of energy disclosed by the first law are relative because the choice of the reference value E_0 is arbitrary. We can assign absolute values by using the theory of special relativity and the concept of (inertial) mass.

In general, and in contrast to energy, 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 either constituents and the electromagnetic field or by chemical reactions, or both, are negligible with respect to the mass of the system. As a result, we establish a very useful tool, the *mass balance*, i.e.,

$$(m_2 - m_1)_{\text{system } A} = m^{A\leftarrow} \quad (3)$$

where $m^{A\leftarrow}$ is the net amount of mass exchanged with the environment of system A . The mass $m^{A\leftarrow}$ is positive if mass flows into A .

4.4. UNITS OF BOTH ENERGY AND MASS

Provide a table of the different units and the conversion factor from one unit to another for both energy and mass.

5. Lecture 4

5.1. 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 thermodynamics, and provides a readily understandable motivation for the 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 its environment. A *steady state* is one that does not change as a function of time despite interactions of the system with its environment. A *nonequilibrium state* is one that changes spontaneously as a function of time, that is, a state that evolves in time without any effects on or interactions with the environment. 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, energy and only energy can be transferred out of a system and affect a mechanical effect without leaving any other net changes in the state of the environment. For example, a charged electricity storage battery can supply energy to an electrical appliance. In contrast, experience shows that, starting from a stable equilibrium state having any value of energy, the mechanical effect just cited is impossible. For example, an internally discharged battery can have the same amount of energy as a charged battery and yet the former cannot energize an electrical appliance. 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 will be introduced in the next section.

6. Lecture 5

6.1. STABILITY AND THE SECOND LAW

To a scientist or engineer familiar with mechanics, the existence of stable equilibrium states at any value of energy is not self-evident. It was first recognized by Hatsopoulos and Keenan [12] as the essence of all correct statements of the second law of thermodynamics. We concur with this recognition.

6.2. SECOND LAW OF THERMODYNAMICS

The *second law* asserts that, among all the states of a system with a given value of energy E , and given values of the amount n of the constituent and of the volume V , there exists one and only one stable equilibrium state.

The existence of a stable equilibrium state for each set of values E , n , V and, therefore, the second law of thermodynamics cannot be derived from the laws of mechanics. In mechanics among all the states of a system with a fixed value of the amount of the constituent and a fixed value of the volume, the only stable equilibrium state is that of lowest energy, that is, the state of least potential energy and zero kinetic energy. In contrast, the second law avers that a stable equilibrium state exists for each value of the energy. It follows that the class of states contemplated by thermodynamics is broader than the class of states contemplated by mechanics.

6.2.1. *Impossibility of Perpetual Motion Machine of the Second Kind*

The existence of stable equilibrium states for various conditions of a system has many theoretical and practical consequences. One consequence is that, starting from a stable equilibrium state of any system, no energy can be extracted to affect solely a mechanical effect while the values of the amount of the constituent and of the volume of the system experience no net changes. If the extraction were possible, the energy could be returned to the system, and accelerate it to a nonzero speed. Thus the stable equilibrium state would have been changed to another state without any effect on the environment. Such a change violates the definition of stable equilibrium. Because the concept of stable equilibrium is part of the second law, such a violation is also a violation of that law. 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.

7. Lecture 6

7.1. ADIABATIC AVAILABILITY

For given values of n and V , another consequence of the two laws is that not all states can be changed to the state of minimum energy of the system by means of interactions which result solely in the rise of a weight — interactions which have solely a mechanical effect on the environment. This is a generalization of the impossibility of a PMM2 because the initial state is not a stable equilibrium state. In essence we prove the existence of another property that we call adiabatic availability and denote by Ψ .

The *adiabatic availability* Ψ_1 of a system in state A_1 represents the largest amount of energy that can be transferred from the system to a weight in a reversible process, as A changes from initial state A_1 to a stable equilibrium state A_0 . The value of Ψ is nonnegative.

7.1.1. Reversible and Irreversible Processes

Among other distinctions, a process may be either reversible or irreversible. A process is *reversible* if it can be performed in at least one way such that both the system and the environment can be restored to their respective initial states. A process is *irreversible* if it is impossible to perform it in such a way that both the system and its environment can be restored to their respective initial states.

7.2. GENERALIZED ADIABATIC AVAILABILITY

The concept of adiabatic availability can be generalized to a reversible process of system A in the course of which the only effect on the environment is the rise or fall of a weight as the system changes from state A_1 with values n_1 and V_1 to a stable equilibrium state A_0 with values n_0 and V_0 . We define the energy exchanged between the system and the weight in the course of the process just cited as *generalized adiabatic availability*. The energy exchanged between the system and the weight is optimum. It is the largest if transferred from the system to the weight, and the smallest if transferred from the weight to the system. For simplicity, we denote generalized adiabatic availability by the same symbol Ψ as adiabatic availability. If energy is transferred out of the system, the adiabatic availability is denoted by a positive number, and if transferred into the system, by a negative number.

Like energy, Ψ is a well-defined property of any system in any state. Unlike energy, neither adiabatic availability nor generalized adiabatic availability is additive. If $n_1 = n_0$ and $V_1 = V_0$, it is noteworthy that the generalized adiabatic availability reduces to the adiabatic availability.

8. Lectures 7 and 8

8.1. ADIABATIC AVAILABILITIES OF A SYSTEM AND A RESERVOIR

Additive properties are very useful because they facilitate the discussion of properties of composite systems — systems that consist of two or more subsystems. In striving to define an additive availability, we investigate the adiabatic availabilities of a composite consisting of a system and of a special reference system called a reservoir. These availabilities are generalizations of the concept of motive power of fire first introduced by Carnot [13]. They are generalizations because he restricted the composite to consist of two reservoirs with fixed values of both the respective constituents and the respective volumes, and we do not use his restrictions.

8.2. MUTUAL STABLE EQUILIBRIUM

If a composite of two or more subsystems is in a stable equilibrium state, the subsystems are said to be in *mutual stable equilibrium*. For example, if system C is in a stable equilibrium state and is a composite of two systems A and B , we say that A is in mutual stable equilibrium with B .

In contrast, if each of two systems is in a stable equilibrium state, their composite is not necessarily in a stable equilibrium state and, therefore, the two systems are not necessarily in mutual stable equilibrium.

8.3. RESERVOIR

A *reservoir* is an idealized kind of system that provides useful reference states both in theory and in applications, and that behaves in a manner approaching the following limiting conditions: (a) it passes through stable equilibrium states only; (b) in the course of finite changes of state, it remains in mutual stable equilibrium with a duplicate of itself that experiences no such changes; and (c) at constant values of both the constituent and the volume of each of two reservoirs initially in mutual stable equilibrium, energy can be transferred reversibly from one reservoir to the other with no net effect whatsoever on the environments of the two reservoirs.

8.4. AVAILABLE ENERGY

We consider a composite of system A in state A_1 , and reservoir R in state R_1 . Without net changes of the values of both the amounts of constituents and the volumes of A and R , we raise the question: What is the largest energy that can be exchanged between the composite and its environment so that the only effect on the latter is the rise of a weight?

The answer is the adiabatic availability of the composite and, therefore, conforms to the following assertions: (a) it is limited and equal to the energy exchanged during a reversible weight process in which system A starts from state A_1 , interacts with both the weight and the reservoir, and ends being in mutual stable equilibrium with the reservoir; (b) it is the same for all reversible weight processes such that system A begins from a given state A_1 and ends in a state in which A and R are in mutual stable equilibrium; (c) it is independent of the initial state of R ; and

(d) it is the same for all reservoirs that are initially in mutual stable equilibrium with R .

We denote this largest value by Ω_1^R , and conclude that Ω^R is a property of the composite of A and R . We call Ω^R *available energy*.

8.5. GENERALIZED AVAILABLE ENERGY

We consider weight processes of a composite of system A and reservoir R in which the values of both the amount of the constituent and of the volume of A experience net changes. For example, system A is in state A_1 with values n_1 and V_1 and, at the end of a weight process of the composite that affects only the elevation of a weight in the environment of the composite, the values are n_0 and V_0 . Again, system A is in state A_2 with values n_2 and V_2 and at the end of the weight process of the composite the values are the same n_0 and V_0 as in the first example. With these specifications, we raise the question: Under the conditions just cited, what is the optimum amount of energy that can be exchanged between the composite and the weight?

The answer is the generalized adiabatic availability of the composite. It is the largest if the energy transfer is from the composite to the weight, and the smallest if the energy transfer is from the weight to the composite. For simplicity, we denote the optimum by the same symbol Ω^R as for available energy, and call it the *generalized available energy* of the composite of A and R . For state A_1 with n_1 and V_1 , and final values n_0 and V_0 , the value of Ω^R is denoted as Ω_1^R . For state A_2 with n_2 and V_2 , and final values again n_0 and V_0 , the value of Ω^R is denoted Ω_2^R . For $n_1 = n_2 = n_0$ and $V_1 = V_2 = V_0$, and a given reservoir R , the generalized available energy is identical with the available energy.

It is noteworthy that generalized available energy is defined for any state of any system regardless of whether the state is steady, unsteady, nonequilibrium, equilibrium, 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, like energy, Ω^R is an additive and nonstatistical property of the composite system of A and R .

8.5.1. Energy and Generalized Available Energy Relations

In principle, given any two states A_1 and A_2 of system A and a reservoir R , we can tabulate the values of the energies E_1 and E_2 , and the generalized available energies Ω_1^R and Ω_2^R . For a process of A alone from state A_1 to state A_2 that affects only the elevation of a weight in the environment of A , that is, a weight process of A and not of the composite of A and R , we can prove the following. *If the process of A alone is reversible, then*

$$E_1 - E_2 = \Omega_1^R - \Omega_2^R ; \quad (4)$$

and if the process of A alone is irreversible, then

$$E_1 - E_2 < \Omega_1^R - \Omega_2^R . \quad (5)$$

9. Lecture 9

9.1. ENTROPY AND ENTROPY BALANCE

Entropy is the concept that distinguishes thermodynamics from all other branches of science and engineering. It is an additional dimension of the space defined by the properties of a system, and has important, strange and unusual characteristics that have attracted the attention of thousands of scientists and engineers, and that have stimulated animated discussions.

9.1.1. Definition of Entropy

A system A in any state A_1 has the two properties: energy E_1 , and generalized available energy Ω_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 the auxiliary reservoir R , a reference state A_0 , with energy E_0 and generalized available energy Ω_0^R , to which is assigned a reference value S_0 , and the expression

$$S_1 = S_0 + \frac{1}{c_R} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)] \quad (6)$$

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 in practically all 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 both macroscopic and microscopic systems, including a system with one particle with only one (translational) degree of freedom, that is, even one particle has entropy; it is not restricted to stable or thermodynamic equilibrium states; it is defined for both stable equilibrium and not stable equilibrium states because both energy and generalized available energy are defined for all states; and most certainly, it is not statistical because both energy and generalized available energy are not statistical.

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.

Because both energy and generalized available energy are additive, entropy is also an additive property. In contrast, whereas energy remains constant in time if the system experiences either a spontaneous process or a zero-net-effect interaction only with a weight, using relations 4 to 6 we prove that entropy remains constant if either of these processes is reversible, and increases if either of these processes is irreversible. These two features are known as *the principle of nondecrease of entropy*.

The spontaneous entropy creation or increase during an irreversible process is called *entropy generated by irreversibility*. It is positive. Like energy conservation,

entropy nondecrease is a time-dependent result which here is obtained without use of the unknown general equation of motion.

9.1.2. Entropy Balance

Like energy, entropy can be exchanged between systems by means of interactions. Denoting by $S^{A\leftarrow}$ the amount of entropy exchanged between system A and the environment 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,

$$(S_2 - S_1)_{\text{system } A} = S^{A\leftarrow} + S_{\text{irr}} \quad (7)$$

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 state that is not stable equilibrium as the constituent tries to conform to both the external and internal forces, and tends towards stable equilibrium.

10. Lecture 10

10.1. STABLE EQUILIBRIUM STATES AND THE STATE PRINCIPLE

An isolated system admits an infinite number of states that share the same values of energy E , amount of constituent n , and volume V . Some of these states are nonequilibrium, some are equilibrium and, according to the second law, one and only one is a stable equilibrium state. It follows that the value of any property of the system in a stable equilibrium state is uniquely determined by the values E , n , V , that is, it can be written as a function of E , n , V only. This result is known as the *stable equilibrium state principle* or simply the *state principle*.

10.2. THE FUNDAMENTAL RELATION

A system in general has an infinite 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 , V or the values of an equivalent set of three other independent properties. In contrast, for states that are not stable equilibrium, the values of E , n , V are not sufficient to specify the values of all independent properties.

In general, one property of great interest is the entropy of stable equilibrium states which, according to the state principle, must satisfy the relation of the form

$$S = S(E, n, V) \quad (8)$$

that is, S must be solely a function of E , n , V . The function $S(E, n, V)$ is called the *fundamental relation*, and is concave — has a negative second partial derivative — with respect to each of the independent variables E , n , V . The entropy of each unique stable equilibrium state is larger than that of any other state with the same values E , n , V . This result is known as the *highest entropy principle*.

Upon solving the fundamental relation for E , we find the *energy relation*, that is, we express the energy as a function of S , n , V

$$E = E(S, n, V) . \quad (9)$$

Traditionally, if the energy of a system in a stable equilibrium state depends only on S , n , V , it is called *internal energy*, and is denoted by U . However, this terminology must not be misconstrued as implying that some systems have both internal and external energy.

10.3. TEMPERATURE, CHEMICAL POTENTIAL, AND PRESSURE

Upon writing the differentials of the fundamental relation and the energy relation, we find

$$dS = \left(\frac{\partial S}{\partial E}\right)_{n,V} dE + \left(\frac{\partial S}{\partial n}\right)_{E,V} dn + \left(\frac{\partial S}{\partial V}\right)_{E,n} dV \quad (10)$$

$$dE = \left(\frac{\partial E}{\partial S}\right)_{n,V} dS + \left(\frac{\partial E}{\partial n}\right)_{S,V} dn + \left(\frac{\partial E}{\partial V}\right)_{S,n} dV \quad (11)$$

Thus, we define

$$T = \left(\frac{\partial E}{\partial S}\right)_{n,V} = \text{temperature}; \quad p = -\left(\frac{\partial E}{\partial V}\right)_{S,n} = \text{pressure};$$

$$\mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} = \text{chemical potential}.$$

Moreover, upon solving equation (10) for dE and comparing the result with equation (11), we find

$$T = \frac{1}{(\partial S/\partial E)_{n,V}}; \quad \mu = -T(\partial S/\partial n)_{E,V}; \quad p = T(\partial S/\partial V)_{E,n}.$$

The concepts of temperature, chemical potential, and pressure are valid only for stable equilibrium states, and are very useful because, if two systems are in mutual stable equilibrium, then the temperature, chemical potential, and pressure of one system is equal to the temperature, chemical potential, and pressure of the other, respectively. In other words, we have temperature equality, chemical potential equality, and pressure equality.

It is noteworthy that either of the differentials

$$dS = dE/T - (\mu/T) dn + (p/T) dV \quad (12)$$

$$dE = T dS + \mu dn - p dV \quad (13)$$

is a mathematical relation between properties of neighboring stable equilibrium states, and not the result of any interactions. Temperature is measured on different scales. The same is true for chemical potential and pressure.

11. Lecture 11

11.1. ENERGY VERSUS ENTROPY GRAPHS

Because they are defined in terms of the values of the amount of the constituent, the volume, and a complete set of independent properties, states can in principle

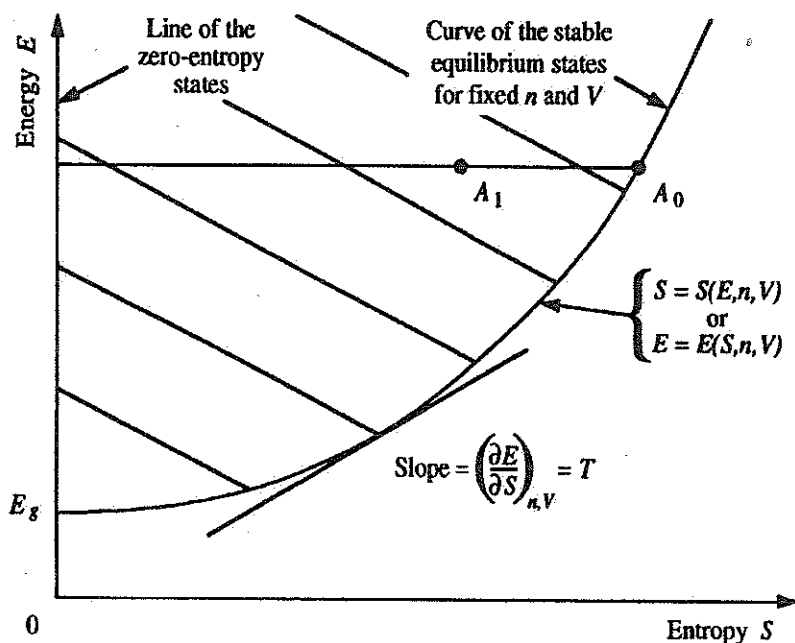


Figure 1. Typical energy versus entropy graph. All concepts of the introductory lectures, including work and heat interactions, can be illustrated on this graph.

be represented by points in a multidimensional geometrical space with one axis for the amount, one for the volume, and one for each independent property. Such a representation, however, would not be enlightening because the number of independent properties is infinite. Nevertheless, useful information can be summarized by first cutting the multidimensional space with a surface corresponding to given values of both the amount of the constituent and the volume, and then projecting the result onto a two-dimensional plane — a plane of two property axes. Here we discuss the energy versus entropy plane which illustrates many of the basic concepts of thermodynamics.

For given values of the amount of the constituent 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.

Each 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 amount of the constituent, 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 amount of the constituent, 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 states implied and required by the second law or, more specifically, the existence of entropy as a property. So mechanics can be regarded as a special case of thermodynamics — zero-entropy physics.

The stable-equilibrium-state curve represents relations $S = S(E, n, V)$ and $E = E(S, n, V)$. Each stable equilibrium state has either the lowest energy for a given entropy, or the highest entropy for a given energy. So, stable equilibrium states can be regarded as either lowest energy physics for a given entropy, or highest entropy physics 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 stable equilibrium state A_0 , the system cannot transfer energy to affect a solely mechanical effect on the environment without net changes in n and V because no state of lower energy exists that has an entropy equal to or greater than the entropy of A_0 . This is a graphical illustration of the impossibility of PMM2. It is sometimes expressed as the nonexistence of a *Maxwellian demon*. The vertical distance of state A_1 from the stable equilibrium state curve is the adiabatic availability Ψ_1 . The vertical distance of A_1 from a tangent to the curve of slope T_R is the available energy Ω_1^R of system A in state A_1 with respect to reservoir R at temperature T_R .

Generation of entropy occurs as an isolated system changes its state spontaneously from A_1 to A_0 . All other aspects of thermodynamics can be illustrated on suitable E versus S , or E versus n , or E versus V graphs.

11.2. THE THIRD LAW OF THERMODYNAMICS

For the given values n, V , the energy E_g is the lowest energy — ground-state 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 amount of the constituent and the volume of a system, there exists one stable equilibrium state with zero temperature.

12. Lecture 12

12.1. INTERACTIONS

Interactions between a system and its environment can have a great variety of effects. Some result in exchange only of energy between the system and its environment at constant system volume. Other interactions result in exchanges of energy and entropy, but neither the amount of the constituent nor the value of the volume are affected. Still others may result in exchanges of energy, entropy, and the constituent, as well as in changes in values of the volume. Such exchanges

result in changing the states of the system and its environment. 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.

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 amount of entropy generation by irreversibility is by specifying each interaction in terms of the net exchanges that it causes at the boundary between the system and its environment, and comparing these exchanges to the changes of properties of the system. For this reason we classify interactions into different categories, such as exchanges involving energy and the constituent but no entropy, and energy and entropy but not the constituent. Two types of interactions are work and heat. An interaction that results in a net exchange of energy between a system and its environment but no exchanges of entropy and the constituent is called a *work interaction*. The amount of energy exchanged is called *work*, and denoted by W^{\rightarrow} . Work W^{\rightarrow} is positive if energy flows out of the system. An interaction that results in net exchanges of energy and entropy but no constituent between the system and an environment at fixed temperature T_Q , that is, a reservoir, and such that the ratio of the amount of energy exchanged and the amount of entropy is equal to T_Q , is called a *heat interaction*. The energy exchanged with the system is called *heat*, and denoted by Q^{\leftarrow} . Heat Q^{\leftarrow} is positive if energy flows into the system.

12.2. PRACTICAL USE OF BALANCES

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

$$(E_2 - E_1)_{\text{system } A} = E^{A\leftarrow} = Q^{A\leftarrow} - W^{A\rightarrow} \quad (14)$$

$$(S_2 - S_1)_{\text{system } A} = S^{A\leftarrow} + S_{\text{irr}} = \frac{Q^{A\leftarrow}}{T_Q} + S_{\text{irr}} \quad (15)$$

$$(m_2 - m_1)_{\text{system } A} = m^{A\leftarrow} = 0 \quad (16)$$

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. The usefulness of balances 12 to 14 is increased if the initial and final states — end-states — of the system are assumed to be stable equilibrium states. Then, the differences $(E_2 - E_1)_{\text{system}}$ and $(S_2 - S_1)_{\text{system}}$ can be expressed in terms of temperatures and pressures, and many practical results can be computed.

13. Concluding Remarks

In our experience with undergraduate teaching in an engineering school, we manage to develop the preceding sequence in the first 12 hours of the course. After these lectures, we proceed with applications of the state principle and of energy, entropy, and mass 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 topics of thermodynamics. 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 thermodynamics and the explicit role of its laws. Second, the students build up much more confidence in all the results if they have seen the precise and rigorous logic that is behind at least for some of them. This is what is missing from traditional expositions.

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