

What is the Second LAW?*

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The thesis of this article is that thermodynamics is a rigorous science, and that the first law and the second law can be stated in an unambiguous and general way so that their implications are concrete and valid for both equilibrium and nonequilibrium states. In this light, we summarize the principles of thermodynamics, and introduce a graphical tool, the energy versus entropy diagram, that is very helpful to explain and grasp the general implications of these principles, especially in the nonequilibrium domain.
[DOI: 10.1115/1.4026379]

Premise

In a recent thermodynamics text, Truesdell [1] identifies several different “second laws”. In a review in 1986, the physicist-philosopher Bunge [2] compiles a list of about twenty ostensibly inequivalent but equally vague formulations of the “second law”. In a manuscript published in 1983, Lindblad [3] gives a large number of different expressions for entropy. No wonder scientists and engineers are puzzled about the foundations of thermodynamics in general, and the second law in particular.

The thesis of this presentation is that thermodynamics is a rigorous science, that its principles can be stated in an unambiguous and general way, and the implications of these principles are concrete and valid for both equilibrium and nonequilibrium states.

In this article, we present a concise summary of the principles of thermodynamics. The summary provides evidence in support of our thesis.

Most of the definitions, statements, and observations presented here, as well as the graphical representation by means of the energy versus entropy diagram, are well familiar to the M.I.T. alumni who took the graduate course taught by the first author during the last twenty years (jointly with the second author during the last six), but are published here for the first time, and cannot be found in any of the hundreds of textbooks on thermodynamics published to date.

Introduction

Thermodynamics is concerned with the instantaneous condition that any material may assume, and the time-dependent evolution of this condition that may occur either spontaneously or as result of interactions with other materials, or both. It is a science with the same objective as the whole of physics and, therefore, subsumes each special branch of physics, such as the theory of mechanics, electromagnetism, and classical thermodynamics, as a special case.

Because of the breadth and depth of its scope, the exposition of thermodynamics requires rigorous consideration of many basic concepts. Some of these concepts are very well known from introductory courses in physics and, for this reason, we assume that ideas such as space, time, velocity, acceleration, mass, force, kinetic energy, and potential energy are well understood and need not be reemphasized. On the other hand, other concepts such as those represented by the terms system, property, state, process, energy, and entropy are sometimes not clearly defined and need special emphasis. In this article, we provide a brief summary of the key concepts, and graphical illustrations of the results.

*Published in the Proceedings of the Fourth International Symposium on Second Law Analysis of Thermal Systems (Rome, Italy, May 25–29, 1987), Edited by M. J. Moran and E. Sciuuba, ASME book I00236, pp. 155–170 (1987). Reprinted with permission.

Systems, Properties and States

A **system** is a collection of constituents which is defined by the following specifications: (a) the type and the range of values of the **amount** of each constituent; for example, 1 kg of water molecules, or between 5 and 10 kg of atmospheric air; (b) the type and the range of values of the **parameters** which fully characterize the external forces that are exerted on the constituents by bodies other than the constituents; for example, the parameters that describe the geometrical shape of an airtight container; and (c) the **internal** forces between constituents such as the forces between water molecules, the forces that promote or inhibit a chemical reaction, the partitions separating constituents in one region of space from constituents in another region, or the interconnections between separated parts. Everything that is not included in the system is called the **environment** or the surroundings of the system.

For a system consisting of r different types of constituents, we denote their amounts by the vector $\underline{n} = \{n_1, n_2, \dots, n_r\}$ where n_1 stands for the amount of the first type of constituent, n_2 for the amount of the second, and so on. For example, the different types of constituents could be: three specific molecules, such as the H_2 , O_2 , and H_2O molecules, with amounts denoted, respectively, by n_1 , n_2 , and n_3 , two specific ions, such as H^+ , O^- , H_3O^+ , and OH^- ions, with amounts denoted, respectively, by n_1 , n_2 , n_3 and n_4 ; four specific ions, such as the H^+ , O^- , H_3O^+ , and OH^- ions, with amounts denoted, respectively, by n_1 , n_2 , n_3 , and n_4 ; three specific elementary particles such as the electron, proton, and neutron particles, with amounts denoted by n_1 , n_2 , and n_3 ; or a single specific field such as the electromagnetic radiation field, with amount denoted by n and equal to unity, $n = 1$.

It is clear that for each set of different types of constituents there are different internal forces between constituents. For example, if only H_2O molecules are considered then the only internal force is that between H_2O molecules. Again, if H_2O , H_2 and O_2 molecules are considered, and the chemical reaction $H_2 + 1/2 O_2 = H_2O$ occurs, the intermolecular forces between all types of molecules must be specified as well as the forces that control the chemical reaction.

For a system with external forces described by s parameters, we denote the parameters by the vector $\underline{\beta} = \{\beta_1, \beta_2, \dots, \beta_s\}$ where β_1 stands for the first parameter, β_2 for the second, and so on. For example, one of the parameters could be the side L or the volume V of a three-dimensional cubic region in space which is enclosed by either the walls of a container or a geometric (as opposed to material) surface chosen to separate the constituents that belong to the system from all the others that do not and are outside the enclosure. Again, another parameter could be the potential ν of a uniform gravitational field in which the constituents are immersed, the potential ψ of an electromagnetic field in which the constituents are floating, or the area a of a two-dimensional surface in space on which the constituents are constrained.

At any instant of time, the amount of each type of constituent and the parameters of each external force have specific values within the corresponding ranges of the system. By themselves,

these values do not suffice to characterize completely the condition of the system at that time. We need, in addition, the values of all the properties at the same instant of time. Each **property** is an attribute that can be evaluated by means of a set of measurements and operations which are performed on the system and result in a value – the **value of the property**. This value is independent of the measuring devices, other systems in the environment, and the history of the system. For example, the instantaneous position of each molecule of a constituent is a property of a system.

For general discussions, we denote properties by the set of symbols P_1, P_2, \dots , and their values by the same symbols, with or without an additional subscript. For example, P_1 may stand for position, P_2 for velocity, and so on. For specific discussions, more often than not we use a different letter for each property, such as E for energy, S for entropy, Ψ for adiabatic availability and Ω for available energy.

Some properties in a given set are independent if the value of each such property can be varied without affecting the value of any other property in the set. Other properties are not independent. For example, speed and kinetic energy of a molecule are not independent properties.

The values of the amounts of all the constituents, the values of all the parameters, and the values of a complete set of independent properties encompass all that can be said at an instant of time about a system and about the results of any measurements or observations that may be performed on the system at that instant of time. As such, the collection of all these values constitutes a complete characterization of the system at that instant of time. We call this characterization at an instant of time the **state** of the system.

Changes of State With Time

The state of a system may change with time either spontaneously due to the internal dynamics of the system or as a result of interactions with other systems, or both. A system that can experience only spontaneous changes of state, i.e., a system that cannot induce any effects on the state of the environment, 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 interaction by means of elastic collisions results in the flow or transfer of momentum from one system to the other.

The relation that describes the evolution of the state of a system as a function of time is called the **equation of motion**. In thermodynamics, the complete equation of motion is not known. For this reason, the description of a change of state is done in terms of the end states, i.e., the initial and the final states of the system, the modes of interactions that are active during the change of state, and conditions that have been established even without the complete knowledge of the 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. The conditions are consequences of the laws of thermodynamics which reflect facets of the equation of motion such as, as we will see, the conditions that energy is conserved and entropy cannot be destroyed.

The end states and the modes of interactions associated with a change of state of a system are said to specify a **process**. Processes may be classified on the basis of the modes of interactions they involve. For example, a process that involves no interactions is called a **spontaneous process**. Again, a process that involves interactions that result in no external effects other than the change in height of a weight (or an equivalent mechanical effect) is called a **weight process**.

Another important classification of processes is in terms of the possibility of annulling all their effects. A process may be either reversible or irreversible. A process is **reversible** if there is a way to restore both the system and its environment to their respective initial states, i.e., if all the effects of the process can be annulled.

A process is **irreversible** if there is no way to restore both the system and its environment to their respective initial states.

It is noteworthy that, in general, a system A that undergoes a process from state A_1 at time t_1 to state A_2 at time t_2 is well-defined at these two times but is not necessarily well-defined during the lapse of time between t_1 and t_2 . The reason is that the interactions which induce the change of state may involve such temporary alterations of internal and external forces that no system A can be defined during the period t_1 to t_2 .

Energy, and Energy Balance

The main consequence of the first law of thermodynamics is that every system A in any state A_1 has a property called **energy** and denoted by the symbol E_1 . In particular, the **first law** asserts that any two states of a system can always be interconnected by means of a weight process and, for a given weight subject to a constant gravitational acceleration, the change in height during such process is fixed uniquely by the two states of the system. The energy E_1 of any state A_1 can be evaluated by means of an auxiliary weight process that interconnects state A_1 and a reference state A_0 to which is assigned a fixed reference energy value E_0 . Energy is an **additive** property. Moreover, energy is **conserved** whenever the system experiences a zero-net-effect weight process or a spontaneous process. Because of additivity, and because any process of a system can always be thought of as part of a zero-net-effect weight process of an overall system consisting of all the interacting systems, the conclusion of energy conservation is of great generality and practical importance.

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 as a result of all the interactions involved in a process that changes the state of A from A_1 to A_2 , an extremely important analytical tool used in all physics and engineering applications is the **energy balance** equation. This equation is based on the additivity and conservation of property energy. It requires that, as a result of a process, the change in the energy of the system from E_1 to E_2 must be equal to the net amount of energy $E^{A\leftarrow}$ transferred into the system, i.e.,

$$E_2 - E_1 = E^{A\leftarrow} \quad (1)$$

We can express the values of energy in absolute terms by using the relation of general relativity

$$E = mc^2 \quad (2)$$

where m is the total mass, E the absolute energy, and c the speed of light in vacuum. When Equation 1 is combined with Equation 2, we find the mass balance equation, i.e.,

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

For most practical applications that involve no transfer of constituents from other systems to system A , the total mass transfer $m^{A\leftarrow}$ is much smaller than either the total m_2 corresponding to E_2 or the total mass m_1 corresponding to E_1 . Thus, the mass of A is taken as fixed and equal to the rest mass m_0 corresponding to the absolute ground-state energy.

Types of States

Because the number of independent properties of a system is very large even for a system consisting of a single particle, and because most properties can vary over a large range of values, the number of possible states of a system is very large. To facilitate the discussion of these states, we find it useful to classify them into different categories with common features based on some criterion, in particular, we find that a classification of states

according to their time evolutions, i.e., according to the way each state changes as a function of time, brings forth many important aspects of physics.

We classify the states of a system into four types: unsteady, steady, nonequilibrium, and equilibrium. Moreover, we further classify equilibrium states into three types: unstable, metastable, and stable.

Unsteady is a state that changes as a function of time because of interactions of the system with other systems. **Steady** is a state that does not change as a function of time despite interactions of the system with other systems in the environment. **Nonequilibrium** is a state that changes spontaneously as a function of time, i.e., a state that evolves as time goes on without any effects on or interactions with any other systems. **Equilibrium** is a state that does not change as a function of time while the system is isolated — a state that does not change spontaneously. **Unstable equilibrium** is an equilibrium state which, upon experiencing a minute and short lived influence by a system in the environment, proceeds from then on spontaneously to a sequence of entirely different states. **Metastable equilibrium** is an equilibrium state that may be changed to an entirely different state without leaving net effects in the environment of the system, but this can be done only by means of interactions which have a finite temporary effect on the state of the environment. **Stable equilibrium** 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.

Starting either from a nonequilibrium or from an equilibrium state that is not stable, a system can be made to raise a weight without leaving any other net changes in the state of the environment. In contrast, if we start from a stable equilibrium state such a raise of a weight is impossible. This impossibility is one of the consequences of the laws of thermodynamics.

Adiabatic Availability and Available Energy

The main consequence of the second law of thermodynamics is that, in general, not all the energy of a system can be transferred to a weight during a weight process. In particular, for each given set of values of the energy, the amounts of constituents and the parameters, the second law asserts the existence of one and only one stable equilibrium state. It also implies that from this state, no energy can be transferred to the weight in a weight process if the given values of amounts of constituents and parameters experience no net change.

Close examination of the question “how much energy can be transferred to a weight in a weight process of a system?” discloses that every system A in any state A_1 has a property called **adiabatic availability**, denoted by the symbol Ψ_1 , equal to the energy transferred to a weight in the course of a reversible weight process that interconnects state A_1 and a stable equilibrium state A_{S1} with the same values of amounts of constituents and parameters as state A_1 . It also discloses the existence of another property called generalized adiabatic availability which is determined in the same manner as the adiabatic availability except that the values of the amounts of constituents and parameters of the final stable equilibrium state differ from those of the state A_1 . Adiabatic availability is not an additive property.

The adiabatic availability of a composite system consisting of a system A in state A_1 , and a given reservoir R fixed once and for all is an additive property called **available energy with respect to reservoir R**, and denoted by the symbol Ω_1^R . A **reservoir** is an idealized kind of system with a behavior that approaches the following three limiting conditions: (1) it passes through stable equilibrium states only; (2) 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 (3) at constant values of amounts of constituents and parameters of each of two reservoirs initially in mutual stable equilibrium, energy can be transferred reversibly from one reservoir to the other with no net effects on

any other system. Two systems are in **mutual stable equilibrium** if their combination is in a stable equilibrium state.

The available energy Ω_1^R of a system A in any state A_1 with respect to a reservoir R is the largest amount of energy that can be transferred to a weight in a weight process for the combination of system A and the reservoir R without changing the values of the amounts of constituents and the parameters of the system and the reservoir.

A generalized available energy may also be defined as a property of a system A in any state A_1 with respect to a reservoir R. It differs from available energy only in that the final state of system A does not correspond to the same values of the amounts of constituents and parameters as state A_1 .

A distinguishing feature of both adiabatic availability and available energy is that neither of these two properties is necessarily conserved in weight processes. Each cannot be created but is destroyed in any process that is irreversible. Said differently, in the course of an irreversible weight process a system loses some of its potential ability to transfer energy to a weight. Whereas energy is conserved, the amount of energy that can be transferred to a weight in a weight process — the potential of a system to perform useful tasks — is not conserved. This potential cannot be created but may be dissipated to a lesser or larger degree depending on whether the process is a little or a lot irreversible. A quantitative measure of irreversibility can be expressed in terms of the property entropy discussed immediately below.

A noteworthy feature of energy, adiabatic availability, and available energy is that these properties are defined for all states of any system, whether they are steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium states.

Entropy, and Entropy Balance

An important consequence of the laws of thermodynamics is that every system A in any state A_1 has a property called **entropy**, and denoted by the symbol S_1 .

This property can be evaluated by means of an auxiliary reservoir R, a reference state A_0 to which is assigned a fixed reference value A_0 , and the expression

$$S_1 = S_0 + C_R^{-1}[(E_1 - E_0) - \Omega_1^R - \Omega_0^R] \quad (4)$$

where C_R is a well-defined constant property of the reservoir (that turns out to be equal to the temperature of the reservoir). Despite the dependence of the values of C_R and $\Omega_1^R - \Omega_0^R$ on the selection of the reservoir, the values of entropy found by means of Equation 4 are independent of the reservoir, i.e., S is a property of system A only, in the same sense that energy E is a property of system A only.

Whereas energy is conserved whenever the system experiences a zero-net-effect weight process, entropy is conserved only when the weight process is reversible. In the course of any irreversible weight process, the system loses part of its potential ability to transfer energy to a weight, and the entropy of the system increases. These conclusions are known as the **principle of entropy nondecrease**. This increase is called **entropy generated by irreversibility** or entropy production due to irreversibility. Entropy is an additive property and can be transferred between systems by means of interactions.

The principle of entropy nondecrease, and the additivity of entropy imply that a change in the entropy of a system A from S_1 to S_2 during any process starting from state A_1 and ending in state A_2 must be balanced by the sum of the net amount of entropy S^{A-} transferred into the system by means of all the interactions of A with the environment, and the positive amount of entropy S^{A-} generated inside A due to the irreversibility of the process, i.e., that

$$S_2 - S_1 = S^{A-} + S_{irr} \quad (5)$$

Equation 5 is called the **entropy balance**, in addition to the energy balance, the entropy balance is an important analytical tool for physics and engineering applications.

Stable Equilibrium States

Another important consequence of the laws of thermodynamics is that any stable equilibrium state and, therefore, the value of any property of the system in a stable equilibrium state is uniquely determined by the values of the energy E , the amounts of constituents n_1, n_2, \dots, n_r , and the parameters $\beta_1, \beta_2, \dots, \beta_s$, i.e., any property P can be written as a function of the form

$$P = P(E, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s) \quad (6)$$

This result, known as the stable-equilibrium-state principle or, simply, the **state principle**, expresses a fundamental physical feature of the stable equilibrium states of any system, and implies the existence of fundamental interrelations among the properties of these states. In general, a 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 only one is stable equilibrium.

Relation 6, when written for property entropy, i.e.,

$$S = S(E, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s) \quad (7)$$

is known as the fundamental stable-equilibrium-state relation for entropy or, simply, the **fundamental relation**. The function $S(E, \underline{n}, \underline{\beta})$ admits of partial derivatives to all orders and, therefore, any difference between the entropies of two stable equilibrium states may be expressed in the form of a Taylor series in terms of differences in the values of the energy, amounts of constituents and parameters of the two stable equilibrium states. In addition, the function $S(E, \underline{n}, \underline{\beta})$ is concave in each of the variables $E, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s$ in the sense that $(\partial^2 S / \partial E^2)_{\underline{n}, \underline{\beta}} \leq 0$, $(\partial^2 S / \partial n_i^2)_{E, \underline{n}, \underline{\beta}} \leq 0$ for each i , and $(\partial^2 S / \partial \beta_j^2)_{E, \underline{n}, \underline{\beta}} \leq 0$ for each j . It is noteworthy that the entropy of each unique stable equilibrium state is larger than that of any other state with the same values of E, \underline{n} , and $\underline{\beta}$. This latter assertion is known as the **highest entropy principle**.

Equation 7 may be solved for E as a function of $S, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s$ so that

$$E = E(S, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s) \quad (8)$$

The function $E(S, \underline{n}, \underline{\beta})$ admits of partial derivatives to all orders and, therefore, any difference between the energies of two stable equilibrium states may be expressed in the form of a Taylor series in terms of differences in the values of the entropy, amounts of constituents and parameters of the two stable equilibrium states.

Each first order partial derivative of either the function $S(E, \underline{n}, \underline{\beta})$ or the function $E(S, \underline{n}, \underline{\beta})$ represents a feature of the family of stable equilibrium states of a system and plays an important role in establishing conditions for mutual stable equilibrium with other systems. Each such derivative is a property defined only for the stable equilibrium states of the system.

The absolute temperature or, simply, the **temperature** T is defined as the inverse of the partial derivative of $S(E, \underline{n}, \underline{\beta})$ with respect to energy, or the partial derivative of $E(S, \underline{n}, \underline{\beta})$ with respect to entropy, i.e.,

$$T = (\partial S / \partial E)_{\underline{n}, \underline{\beta}}^{-1} = (\partial E / \partial S)_{\underline{n}, \underline{\beta}} \quad (9)$$

The **total potential of the i -th constituent** μ_i , is defined by either of the two relations

$$\mu_i = (\partial E / \partial n_i)_{S, \underline{n}, \underline{\beta}} = -T(\partial S / \partial n_i)_{E, \underline{n}, \underline{\beta}} \quad (10)$$

The **generalized force conjugated to the j -th parameter** f_j is defined by either of the two relations

$$f_j = (\partial E / \partial \beta_j)_{S, \underline{n}, \underline{\beta}} = -T(\partial S / \partial \beta_j)_{E, \underline{n}, \underline{\beta}} \quad (11)$$

When volume V is a parameter, the negative of the generalized force conjugated to V is called **pressure**, denoted by p , and given by either of the two relations

$$p = -(\partial E / \partial V)_{S, \underline{n}, \underline{\beta}} = T(\partial S / \partial V)_{E, \underline{n}, \underline{\beta}} \quad (12)$$

Equality of temperatures of two systems is a necessary condition for the two systems to be in mutual stable equilibrium. Equality of total potentials of a component common in two systems is a necessary condition for the two systems to be in mutual equilibrium if that component in each of the two systems can be changed over a range of values. Equality of pressures of two systems, each having volume as a parameter, is another necessary condition for the two systems to be in mutual stable equilibrium if the volume of each system can be changed over a range of values.

Work and Work Interactions

Interactions result in the exchange of properties across the boundaries of the interacting systems. Various combinations of exchanges are used to classify interactions into different categories.

An interaction between two systems that results in a transfer of energy between the two systems without any transfer of entropy is classified as a **work interaction**, and the amount of energy exchanged as a result of such an interaction as **work**. All interactions that result in the exchange of entropy between the interacting systems are called **nonwork interactions**.

A process of a system experiencing only work interactions is called an **adiabatic process**. Any process that involves nonwork interactions is called nonadiabatic.

In the course of an adiabatic process, system A changes from state A_1 to state A_2 , the energy exchange $(E^{A \leftarrow})^a$ equals the negative of the work done on the environment $W^{A \rightarrow}$ i.e., $(E^{A \leftarrow})^a = -W^{A \rightarrow}$, and the entropy exchange $(S^{A \leftarrow})^a = 0$ where the superscript "a" denotes that the process of A is adiabatic. Therefore, the energy and entropy balances are

$$(E_2 - E_1)^a = -W^{A \rightarrow} \quad (13)$$

$$(S_2 - S_1)^a = S_{\text{irr}} \quad (14)$$

A special example of a nonwork interaction that is entirely distinguishable from work is an interaction between two systems, initially differing infinitesimally in temperature, that results in a transfer of energy and a transfer of entropy between the two systems such that the ratio of the amount of energy transferred to the amount of entropy transferred equals the almost common temperature of the interacting systems. It is called a **heat interaction**, and the amount of energy transferred as a result of such an interaction **heat**.

Often, in applications, a system A consists of many subsystems, one of which A' is in a stable equilibrium state at a temperature T_Q . Similarly, a system B consists of many subsystems, one of which B' is in a stable equilibrium state at temperature almost equal to T_Q . If the two subsystems A' and B' experience a heat interaction, then we say that systems A and B experience a heat interaction at temperature T_Q , even though A and B are not necessarily in stable equilibrium states.

In the course of a process that involves only a heat interaction at temperature T_Q , system A changes from state A_1 to state A_2 , the energy exchange is $(E^{A \leftarrow})^h = Q^{A \leftarrow}$, and the entropy exchange

$(S^{A\leftarrow})^h = Q^{A\leftarrow}/T_Q$ where the superscript “h” denotes that the process of A involves heat interactions only. Therefore, the energy and entropy balances are

$$(E_2 - E_1)^h = Q^{A\leftarrow} \quad (15)$$

$$(S_2 - S_1)^h = Q^{A\leftarrow}/T_Q + S_{\text{irr}} \quad (16)$$

If a process of a system A involves both work and heat but no other interactions, the energy and entropy balances for A are

$$E_2 - E_1 = Q^{A\leftarrow} - W^{A\rightarrow} \quad (17)$$

$$S_2 - S_1 = Q^{A\leftarrow}/T_Q + S_{\text{irr}} \quad (18)$$

or, for differential changes,

$$dE = \delta Q^{A\leftarrow} - \delta W^{A\rightarrow} \quad (19)$$

$$dS = \delta Q^{A\leftarrow}/T_Q + \delta S_{\text{irr}} \quad (20)$$

Work and heat interactions are most frequently encountered in engineering applications.

A noteworthy observation emerges very clearly from our presentation so far, namely, that the widespread jargon by which the energy balance equation is called “the first law” and the entropy balance equation “the second law”, is incorrect and misleading, indeed, it should suffice to note that the main consequence of the first law is the very existence of the additive property energy, and that the definition of entropy and the entropy balance equation require both the first and the second laws, as well as many other important auxiliary concepts.

Graphical Representations on the Energy Versus Entropy Diagram

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 of any system is indefinitely large. Nevertheless, useful information can be summarized by first cutting the multidimensional space with a plane 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 with two property axes. One such plane that illustrates many of the basic concepts of thermodynamics is the energy versus entropy plane.

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 multidimensional state space of the system onto the E versus S plane. This projection must have the shape of the cross-hatched area shown in Figure 1, namely, all the states that share the given characteristics have property values that project on the area between the two heavy lines – the vertical line denoted as the line of the zero-entropy states and the curve denoted as the curve of the stable equilibrium states.

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

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

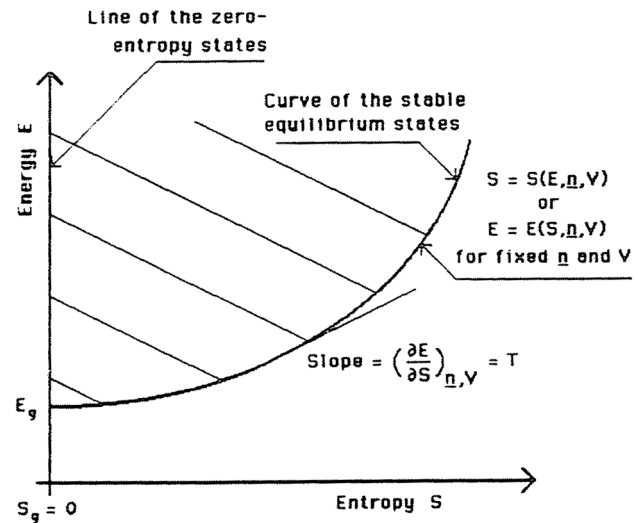


Fig. 1

This projection of states on the E versus S plane is novel because it includes both stable equilibrium states and other states that are not stable equilibrium whereas, usually, graphical representations of thermodynamic relations are restricted to stable equilibrium states only

Zero Entropy Line. The line of the zero-entropy states corresponds to all the states that have the least amount of entropy. This amount can be assigned the value zero because no states exist with lower entropy. Thus, entropy has absolute values greater than or equal to zero. It turns out that the zero-entropy line represents all the states that are defined in mechanics (classical or quantum) without concern about the laws of thermodynamics. So mechanics can be thought of as a special case of thermodynamics, namely, as zero-entropy physics.

Lowest Energy States. For the given values of the amounts of constituents and the volume, the lowest energy of the system is E_g . It corresponds to a unique stable equilibrium state having zero entropy and zero temperature — the slope from above of the stable-equilibrium-state curve at point E_g is equal to zero. The slope from below of the curve at point E_g is indeterminate because no states and, therefore, no curve of stable equilibrium states exist for $S < 0$.

The energy E_g is the lowest energy for which the system can exist with the given types and amounts of constituents, and for the given value of the volume. For example, if the system consists of one hydrogen molecule in a small container, E_g would be the smallest value of the energy of the hydrogen molecule. The smallest energy of two hydrogen atoms in the same container or two protons and two electrons in the same container would clearly differ from E_g . For other values of the amounts of the constituents and the volume, the lowest energy state will be different from that in Figure 1 but still a stable equilibrium state with zero entropy and zero temperature.

The Fundamental Relation. The stable-equilibrium-state curve can be regarded as representing either the convex stable equilibrium state relation E versus S or, equivalently, the concave fundamental relation S versus E , both for the given values of the amounts of constituents and the volume. It is a single-valued relation because for each set of values $E, n,$ and V there is one and only one stable equilibrium state and, therefore, a unique value of S .

The shape of the stable-equilibrium-state curve is convex as shown because this is the only shape consistent with the results

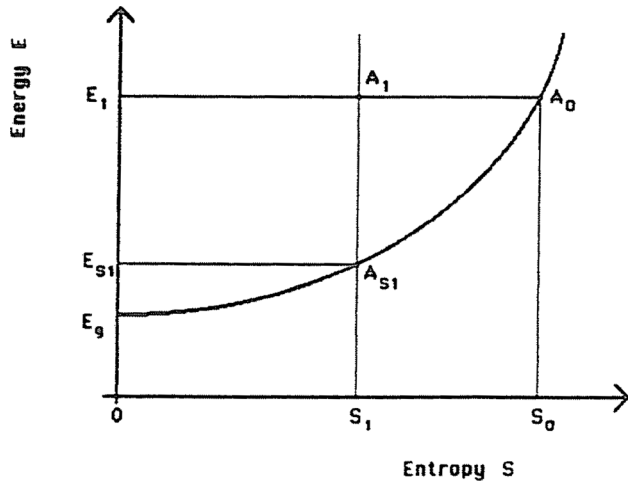


Fig. 2

derived from the laws of thermodynamics, and that we summarize below with reference to Figure 2.

Each Stable Equilibrium State is a State of Lowest Energy Among all The States With the Same Values of S , \underline{n} , and V . For each set of values S , \underline{n} , and V , the stable equilibrium state A_{S1} on the vertical line $S=S_1$ is the state of lowest energy – no states exist below A_{S1} that correspond to the same values of \underline{n} and V , and that lie on the line $S=S_1$. State A_{S1} can be reached starting from any state A_1 on the line $S=S_1$ by means of a reversible weight process without net changes in \underline{n} and V . Indeed, in such a process the net change in the entropy of the system is zero, $S_{S1}=S_1$ and the energy E_1-E_{S1} is transferred out from the system to the weight.

Each Stable Equilibrium State is a State of Highest Entropy Among all the States With the Same Values of E , \underline{n} and V . For each set of values E_1 , \underline{n} , and V , the stable equilibrium state A_0 on the horizontal line $E=E_1$ is the state of highest entropy – no states exist beyond A_0 that correspond to the same values of \underline{n} and V and that lie on the line $E=E_1$. In an isolated system – a system experiencing no interactions – state A_0 can be reached starting from any state A_1 on the line $E=E_1$ by means of a spontaneous change of state. Any such spontaneous process would be irreversible because it entails an increase in the entropy of the system without any effects on the environment.

Temperature is Positive and Increasing with Energy. Because each stable equilibrium state is unique, the temperature $(\partial E/\partial S)_{\underline{n},V}$ at each point on the convex boundary is uniquely defined. Temperature is not defined for states that are not stable equilibrium because then E depends on more variables than S , \underline{n} , and V and, therefore, more quantities should be kept fixed while finding the partial derivative of E with respect to S . More importantly, however, even if the variables in addition to S , \underline{n} , and V were specified, the partial derivative of E with respect to S would not be the quantity that enters the temperature equality requirement for systems in mutual stable equilibrium and, therefore, such a derivative would not have the same meaning as the absolute temperature of thermodynamics.

Perpetual Motion of the Second Kind. Starting from a stable equilibrium state A_{S1} on the convex boundary $E_g A_{S1} A_0$, the system cannot transfer energy to a weight without net changes in the values of the amounts of constituents and the volume because no state of lower energy exists that has an entropy equal to or larger than the entropy of state A_{S1} . Indeed, if energy were transferred to a weight, the energy of the system would be reduced. But starting from state A_{S1} all states with smaller energy have also smaller entropy. Because the weight receives only energy, and entropy cannot decrease by itself, it follows that no such transfer can occur

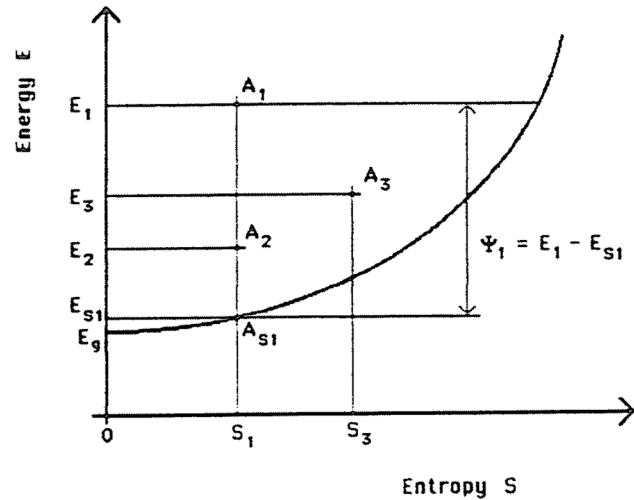


Fig. 3

under the conditions specified. This feature of the graph represents the impossibility of perpetual motion machines of the second kind. This impossibility is sometimes expressed as the nonexistence of a Maxwellian demon, the nonexistence of a superbeing that would be capable of extracting energy but no entropy from a stable equilibrium state without affecting \underline{n} and V .

Classical Thermodynamics. For each set of given values of amounts of constituents and volume, the convex boundary $E_g A_{S1} A_0$ represents the corresponding stable equilibrium states. These are the states considered in classical thermodynamics, which is sometimes also called “thermostatistics” because it contemplates only states that are equilibrium. These states are often referred to in the literature as the thermodynamic equilibrium states. So classical thermodynamics can be thought of as another special case of thermodynamics, namely, as highest-entropy physics.

Adiabatic Availability. For a given state A_1 the energy $E_1 - E_{S1}$ shown graphically in Figure 3 is equal to the adiabatic availability Ψ_1 of A_1 because the change of state from A_1 , to A_{S1} represents the change specified in the definition of Ψ_1 . We see from the figure that, in general, is smaller than the energy of the system above the ground state energy, $E_1 - E_g$. It varies from $E_1 - E_g$ to zero as the entropy S_1 of the state varies from zero to the highest value that is possible for the set of values E_1 , \underline{n} and V . So entropy affects the usefulness of the energy of a system, i.e., the larger the entropy for given values of E , \underline{n} and V , the smaller the adiabatic availability. This limitation on the amount of energy that can be transferred from a system to a weight in a weight process without net changes in the values of \underline{n} and V is a consequence of the laws of thermodynamics of paramount theoretical importance and with many practical implications.

For given values of \underline{n} and V , we see graphically from Figure 3 that stable equilibrium states, such as for example state A_{S1} , have zero adiabatic availability, and that any state with nonzero adiabatic availability cannot be stable equilibrium.

Work in an Adiabatic Process. In an adiabatic process without net changes in amounts and volume, the work done by the system starting from state A_1 and ending in a state different from A_{S1} (Figure 3) is always smaller than the adiabatic availability Ψ_1 .

If the process is reversible, the final state A_2 must have entropy $S_2=S_1$, and energy $E_2 > E_{S1}$. Therefore,

$$(W^{A \rightarrow})_{\text{rev}} = E_1 - E_3 < E_1 - E_{S1} = \Psi_1 \quad (21)$$

If the process is irreversible, the final state A_3 must have entropy $S_3 > S_1$. But for $S_3 > S_1$, the graph shows that A_3 must have energy $E_3 > E_{S1}$ and, therefore,

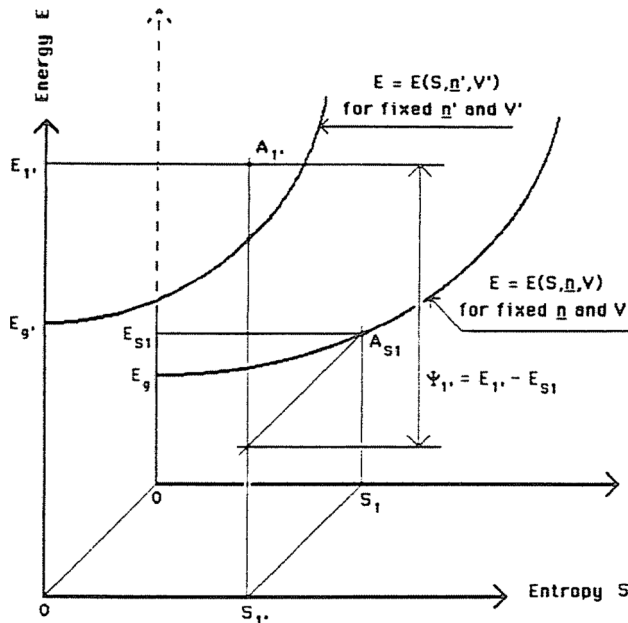


Fig. 4

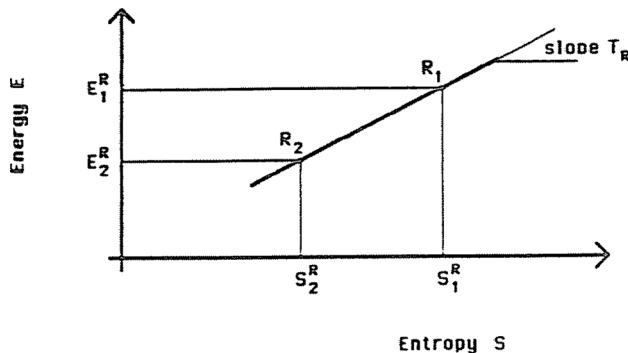


Fig. 5

$$(W^{A \rightarrow})_{\text{irr}} = E_1 - E_3 < E_1 - E_{S1} = \Psi_1 \quad (22)$$

Here, the entropy increase $S_3 - S_1$ is not supplied by another system because the process is adiabatic and, therefore, is generated by irreversibility

Generalized Adiabatic Availability. The generalized adiabatic availability is illustrated graphically in Figure 4. For a given state $A_{1'}$ with values of amounts n' and volume V' , the energy $E_{1'} - E_{S1}$ is equal to the generalized adiabatic availability $\Psi_{1'}$ of $A_{1'}$ with respect to given values \underline{n} of the amounts and V of the volume which may differ from n' and V' , respectively

Available Energy. The E^R versus S^R diagram of a reservoir R is just a straight line of slope T_R (Figure 5) because the reservoir passes through stable equilibrium states only, and has a constant temperature. It is noteworthy that, for very small values of entropy, no system can behave as a constant nonzero temperature reservoir because as entropy approaches zero, the temperature of any system must also approach zero. Moreover, no system at zero temperature can be regarded as a reservoir because its entropy cannot be both decreased and increased, and because for a finite entropy increase the temperature becomes greater than zero.

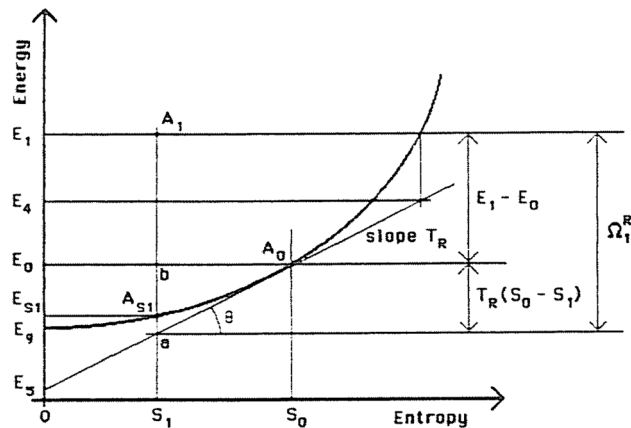


Fig. 6

Given the E versus S diagram of a system A with specified values of amounts of constituents and volume, and a reservoir R at temperature T_H , we can draw a line of slope T_R tangent to the convex stable-equilibrium-state curve of system A, i.e., tangent to the curve $E_g A_{S1} A_0$ in Figure 5. The point of tangency A_0 represents the state A_0 in which system A is in mutual stable equilibrium with the reservoir because in state A_0 the system has a temperature $T_0 = (\partial E / \partial S)_{n, V}$ and, therefore, equal to the temperature T_R of the reservoir. In state A_0 the system has energy E_0 and entropy S_0 .

The tangent is also useful in providing a way to represent graphically the available energy of any state of A. Specifically, for a given state A_1 the vertical distance of point A_1 , from the tangent, i.e., the energy $E_1 - E_a$ represents the available energy Ω_1^R of A_1 with respect to reservoir R.

Indeed, with respect to reservoir R, the available energy Ω_1^R of state A_1 with energy E_1 and entropy S_1 is given by the relation

$$\Omega_1^R = E_1 - E_0 - T_R(S_1 - S_0) \quad (23)$$

because the available energy Ω_0^R of state A_0 is zero. We recall that the available energy Ω_1^R equals the work that would be done in the course of a reversible weight process for the combination of systems A and R in which A would end in state A_0 (Figure 5) and R would change from state R_1 to state R_2 (Figure 5).

The term $E_1 - E_0$ in the right-hand side of Equation 23 is the length bA_1 in Figure 6, i.e., the negative of the change in energy of system A as it goes from state A_1 to state A_0 . The term $-T_R(S_1 - S_0)$ is the length ab because $ab = (bA_0) \tan \theta = (S_0 - S_1)T_R$. Of course ab is also equal to the negative of the change in energy $E_1^R - E_2^R$ of the reservoir as it goes from state R_1 to state R_2 (Figure 5). Thus, the length $aA_1 = bA_1 + ab$ is indeed the negative of the energy change of the combination of A and R and, therefore, the available energy Ω_1^R of state A_1 .

The graphs in Figures 5 and 6 also account for the entropy changes that correspond to any reversible process that yields the available energy. They show that the change in entropy $S_0 - S_1$ of system A is equal and opposite the change in entropy $S_2^R - S_1^R$ of the reservoir R.

By comparing the graphical representations for Ψ_1 and Ω_1^R (Figures 3 and 6), we see that in general the available energy Ω_1^R is greater than the adiabatic availability Ψ_1 . We also see that Ω_1^R can be greater than the energy of the system above the ground state energy, $E_1 - E_g$. For states with energy E_1 , the available energy varies from the largest value $E_1 - E_g$ to the lowest value $E_1 - E_4$ depending on the entropy S_1 of state A_1 , i.e., depending on whether the entropy is zero or the largest for the given E_1 , respectively.

It is noteworthy that although the available energy can be extracted as a result of an adiabatic process for the combination of systems A and R, the processes experienced by both A and R are

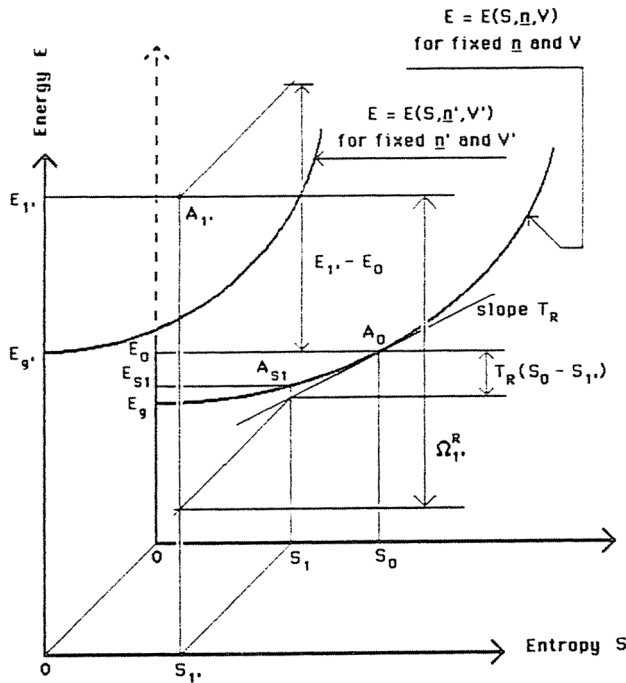


Fig. 7

not necessarily adiabatic because they may involve exchanges of both energy and entropy. In fact, it is precisely the exchange of entropy between A and R that results in sometimes the available energy being greater than the energy of A, or in getting work even when A is in a stable equilibrium state, provided that A and R are not initially in mutual stable equilibrium. In this sense, the reservoir acts as a source or sink of entropy for A. Of course, this entropy exchange between A and R is always accompanied by a definite energy exchange because the reservoir must change both its entropy and its energy as it passes from stable equilibrium state to stable equilibrium state.

One of the many ways of extracting the available energy of, say, state A_1 (Figure 6) is as follows. We first use machinery that interacts reversibly and adiabatically with A only, and extracts the adiabatic availability Ψ_1 .

Thus, system A is brought to stable equilibrium state A_{S1} . At this state, the system is in general at a temperature different from that of the reservoir. Next, we connect the system to the reservoir via reversible heat engines that heat the system to temperature T_R while producing work. Thus, the total work done Ω_1^R is greater than Ψ_1 .

Generalized Available Energy. For a given state $A_{1'}$ with values of amounts n' and volume V' , the generalized available energy $\Omega_{1'}^R = E_{1'}$ with respect to reservoir R and values n and V is represented graphically in Figure 7 and given by the relation

$$\Omega_{1'}^R = E_{1'} - E_0 - T_R(S_{1'} - S_0) \quad (24)$$

where in state A_0 system A is in mutual stable equilibrium with the reservoir, and has values n and V that may differ from n' and V' , respectively, of state $A_{1'}$.

Examples of Work Interactions. Graphical illustrations of work-only interactions between two systems A and B are provided by Figure 8. The combination of A and B is isolated and immersed in a vacuum, so that both A and B can change volume with no external effects. Moreover, the process for each system is reversible. Accordingly, the energy change of A is equal and opposite to the energy change of B, and the entropy changes of both

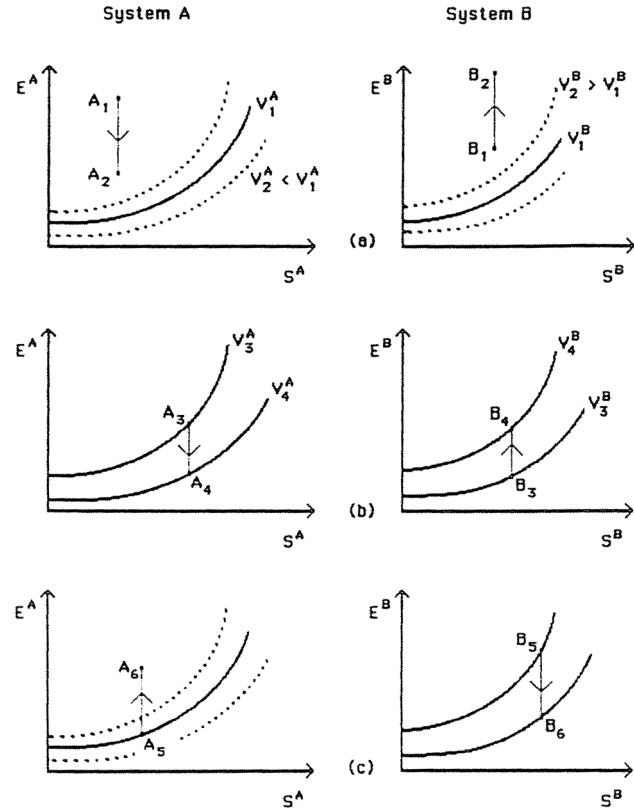


Fig. 8

A and B are zero because a work interaction does not transfer any entropy and the processes for both A and B are reversible.

As a result of the interaction depicted in Figure 8a, the state of A changes from state A_1 to state A_2 and that of B from state B_1 to state B_2 , none being a stable equilibrium state. Moreover, the volume of either system A, or system B or both may or may not change.

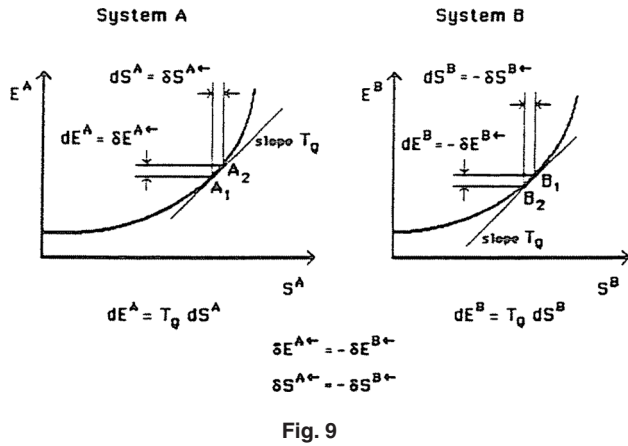
As a result of the interaction shown in Figure 8b, the state of A changes from A_3 to A_4 and that of B from B_3 to B_4 , all being stable equilibrium states. Here the volume of system A changes from V_3^A to V_4^A , and the volume of system B from V_3^B to V_4^B .

As a result of the interaction shown in Figure 8c, the state of A changes from stable equilibrium state A_5 to state A_6 that is not stable equilibrium and may or may not have a different volume than A_5 , whereas the state of B changes from state B_5 to state B_6 both being stable equilibrium states, but with different volumes V_5^B and V_6^B .

For the conditions specified in Figures 8a and 8c, the processes for systems A and B could evolve into irreversible processes because some of the final states of A and B are not stable equilibrium and, therefore, the potential exists for spontaneous entropy creation within the systems. In the example of Figure 8a, irreversibility could occur in either A, or B, or both because state A_2 , or state B_2 , or both could evolve spontaneously towards the corresponding stable equilibrium states. Again, in the example of Figure 8c, irreversibility could occur in A but not in B because only state A_6 could evolve spontaneously, whereas stable equilibrium state B_6 could not.

The processes in Figure 8b cannot become irreversible because the final states of both A and B are stable equilibrium states and, therefore, each has the highest entropy compatible with the corresponding energy.

These simple examples illustrate the well known fact that spontaneous creation of entropy by irreversibility can occur if and only if the system experiences a departure from stable equilibrium.



Examples of Heat Interactions. Graphical illustrations of heat-only interactions between two systems A and B are provided in Figures 9 and 10. In each illustration we assume that the combination of A and B is isolated and that the processes for both systems are reversible. Therefore, the changes in energy and entropy of system A are equal and opposite to the changes in energy and entropy of system B, respectively

As a result of the heat interaction shown in Figure 9, system A changes from state A_1 to state A_2 , system B from state B_1 to state B_2 , all being stable equilibrium states, without net changes in values of amounts of constituents and volumes. The temperatures of A and B are almost equal to T_Q . The two systems exchange energy and entropy. The ratio of the energy exchanged to the entropy exchanged is equal to the common temperature. Because the final states are stable equilibrium, no spontaneous changes of state can occur and, therefore, no entropy can be generated by irreversibility.

As a result of the interaction shown in Figure 10, system A changes from state A_1 to state A_2 , system B from state B_1 to state B_2 , none of which is a stable equilibrium state. However, systems A and B each contain a subsystem A' and B' changing from stable equilibrium states A'_1 and B'_1 to stable equilibrium states A'_2 and B'_2 , respectively, all with temperatures almost equal to T_Q . Thus, the interaction between subsystems A' and B' is of the same kind as that sketched in Figure 9. When viewed as an interaction between systems A and B, however, it is clear that the interaction may be followed by irreversible spontaneous rearrangements of energy and entropy between either A' and other subsystems of A, or B' and other subsystems of B, or both.

Examples of Other Nonwork Interactions. Nonwork interactions that are not heat between two systems A and B are illustrated in Figure 11 where the combination of A and B is isolated and all processes are assumed to be reversible.

As a result of the interaction shown in Figure 11a, the energy of system A decreases but its entropy increases as A changes from state A_1 to state A_2 and, correspondingly, the energy of system B increases but its entropy decreases as B changes from state B_1 to state B_2 . It is clear that this interaction is not heat in the strict sense of the example in Figure 9 because neither system A nor system B pass through stable equilibrium states. It is not heat even in the generalized sense of the example in Figure 10 because the ratio of the energy exchanged to the entropy exchanged is negative.

As a result of the interaction shown in Figure 11b, the energy and the entropy of system A are both decreased as A changes from non-equilibrium state A_3 to stable equilibrium state A_4 and, correspondingly, the energy and entropy of system B are both increased as B changes from stable equilibrium state B_3 to non-equilibrium state B_4 . Assuming that the temperatures T_4 and T_3 of stable equilibrium states A_4 and B_3 are not equal, then the interac-

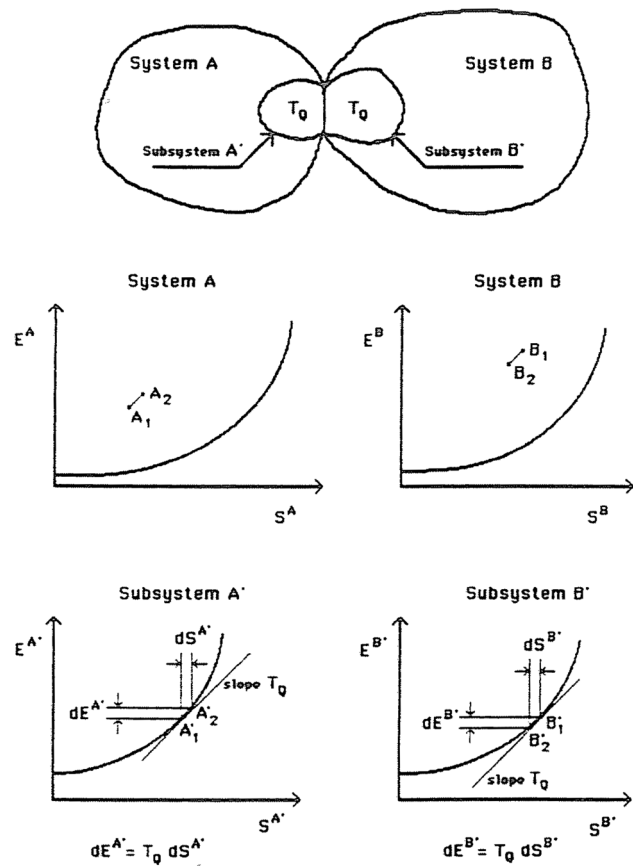


Fig. 10

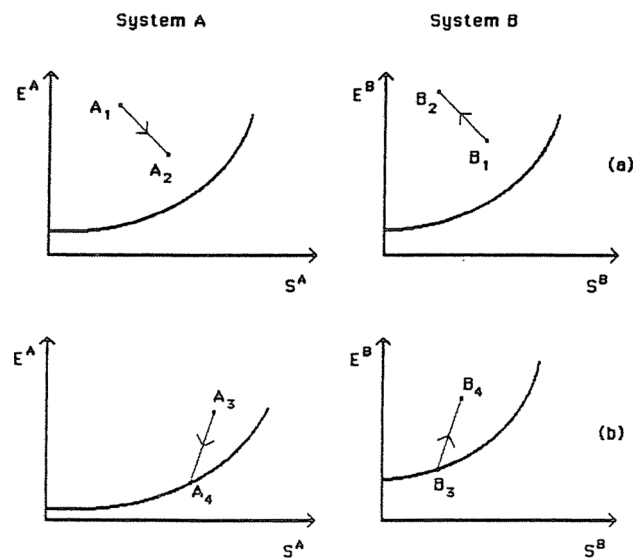


Fig. 11

tion cannot be heat in the strict sense illustrated in Figure 9. It is not heat even in the generalized sense represented in Figure 10 because, even if the exchanges occurred between two subsystems A' and B' passing through stable equilibrium states, the temperatures of these two subsystems are not almost equal to each other.

The reason is that the temperature of A' must be equal to T_A , and that of B' to T_B because in state A_4 subsystem A is in mutual stable equilibrium with the other subsystems of A, and in state B_3 subsystem B' is in mutual stable equilibrium with the other subsystems of B.

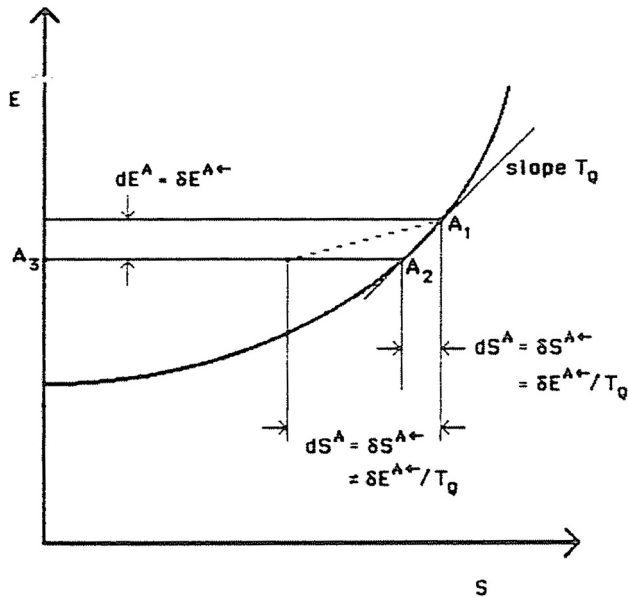


Fig. 12

All the processes represented in Figure 11 could evolve into irreversible processes. For example, in Figure 11a, irreversibility could occur in either system A, or system B, or both because the final states of both A and B are not stable equilibrium. Again, in Figure 11b, irreversibility could occur only in system B because the final state is not stable equilibrium, but not in system A because the final state A_4 is stable equilibrium.

The need for the distinction between heat and other types of nonwork interactions is illustrated by the changes of state shown in Figure 12. System A is initially in a stable equilibrium state A_1 at temperature T_Q . As a result of interactions involving no net changes in values of amounts of constituents and volume, A decreases its energy by an amount $\delta E^{A\leftarrow}$. As the graph illustrates, this change in energy is consistent with each of the final states on the line A_2A_3 . Except for state A_2 , every state on this line corresponds to a transfer of entropy $\delta S^{A\leftarrow}$ different from $\delta E^{A\leftarrow}/T_Q$. Therefore, either we call heat all the interactions that involve an exchange of both energy and entropy, but then we cannot use the relation $\delta Q^{A\leftarrow} = T_Q \delta S^{A\leftarrow}$, i.e., $\delta E^{A\leftarrow} = T_Q \delta S^{A\leftarrow}$, for all these interactions, or we reserve the term heat for interactions for which $\delta Q^{A\leftarrow} = T_Q \delta S^{A\leftarrow}$, and then we need the term nonwork for interactions that involve exchanges of both energy and entropy, and we must realize that heat is only one special kind of nonwork interaction. It is the latter choice that has been made in the present exposition of thermodynamics.

Optimum Changes in Available Energy. Figure 13 is a graphical illustration of the result that the optimum amount of energy that can be exchanged between a weight and a system A in combination with a reservoir R as A changes from state A_1 , to state A_2 equals the change in available energy between these two states.

In Figure 13, available energies are evaluated with respect to the values \underline{n} and V of the amounts of constituents and the volume, for which system A is in mutual stable equilibrium with reservoir R in states A_0 . We have already shown that the length $A_1a = \Omega_1^R$, and is the largest amount of energy that can be transferred to the weight as system A changes from state A_1 to state A_0 in a weight process for the combination of A and the reservoir R. Similarly, the negative of the length A_2b equals the negative of Ω_2^R , and is the smallest amount of energy that must be transferred from the weight to the combination of A and R in order to change system A from state A_0 to state A_2 . Accordingly the difference $\Omega_1^R - \Omega_2^R$ depicted by the length A_1c is the optimum amount of energy exchanged with the weight as A changes from A_1 to A_2 , where

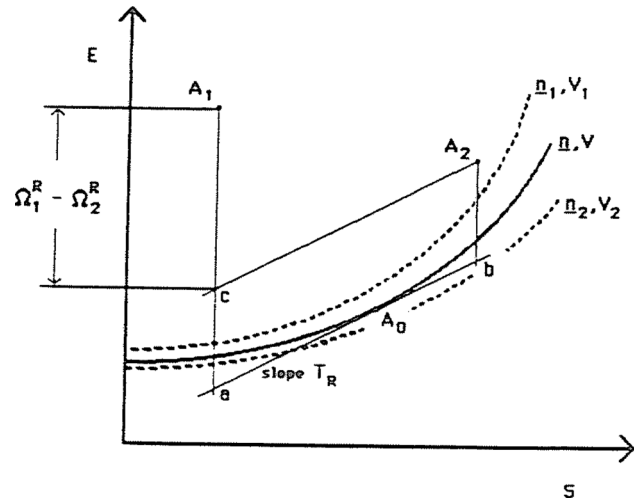


Fig. 13

point c is determined as the intersection of the vertical line A_1c and the line A_2c which passes through A_2 and has slope equal to T_R , the temperature of the reservoir.

It is noteworthy that states A_1 and A_2 need not have the same values of amounts of constituents and volume, indeed, Figure 13 must be viewed as the superposition of three E versus S diagrams for system A, corresponding, respectively, to the values \underline{n}_1, V_1 of state A_1 , the values \underline{n}_2, V_2 of state A_2 , and the values \underline{n}, V chosen as reference values to evaluate available energies. The optimum amount of energy exchanged with the weight, $\Omega_1^R - \Omega_2^R$, can be positive, negative, or zero. If it is positive, then $\Omega_1^R - \Omega_2^R$ corresponds to the highest work that the combination of A and R can do as a result of an adiabatic process for the combination in which A changes from state A_1 to state A_2 . If it is negative, then $\Omega_1^R - \Omega_2^R$ corresponds to the lowest work that must be done on the combination of A and R in an adiabatic process for the combination in order to change system A from A_1 to A_2 .

Effects of Irreversibility on Available Energy We have already illustrated the adverse effects of irreversibility in adiabatic processes for system A. Figure 14 provides a graphical explanation of the adverse effects of irreversibility on the capacity to do work of a system A that is in combination with a reservoir R.

To make ideas specific, we consider a reversible adiabatic process for the combination of A and R in which the state of A changes from state A_1 , to state A_3 having energy $E_3 = E_2$. The work done by the combination is given by the length A_1d on the vertical line A_1ca . Because state A_3 is not stable equilibrium, it could change spontaneously to state A_2 thus generating an amount of entropy $S_{irr} = S_2 - S_3$ due to irreversibility. During this spontaneous change of state, no work is done by either A or the combination of A and R, and the energies of both A and R remain fixed. However, had state A_2 been reached as a result of a reversible adiabatic process for the combination of A and R, the work done would have been given by the length A_1c which is greater than A_1d . We can readily verify that the difference $cd = A_1c - A_1d$ is equal to $T_R S_{irr}$, and so confirm again the adverse effects of irreversibility.

Modified Statement of the Second Law

To obtain the results just summarized, the second law must be stated with the proviso that "starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process."

Among other implications, this proviso results in the conclusion that for each given set of values of amounts of constituents and

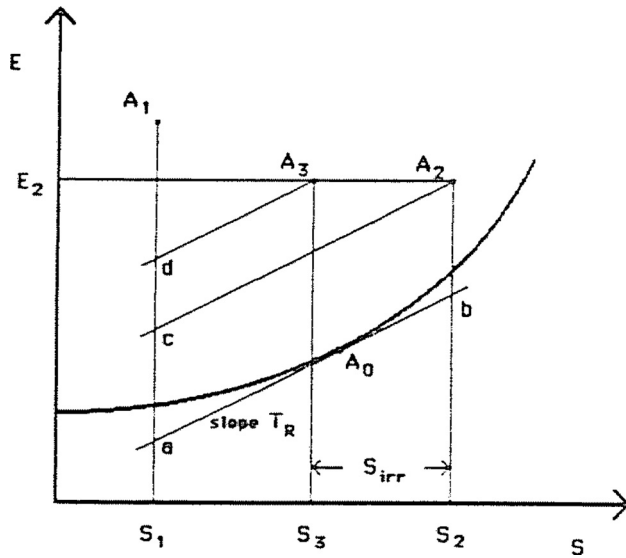


Fig. 14

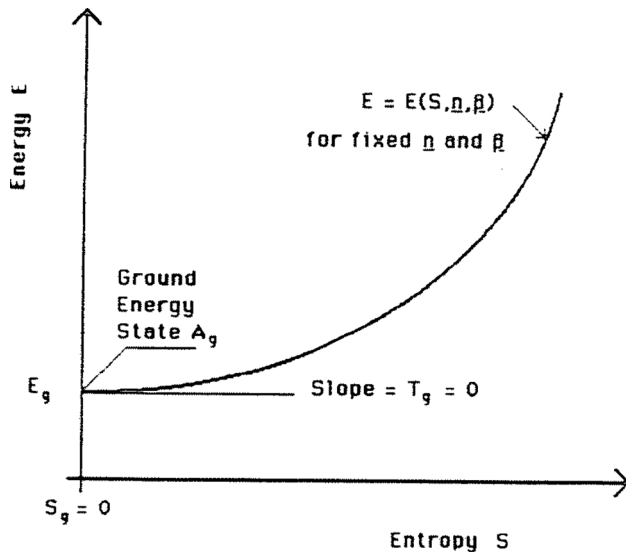


Fig. 15

parameters a system admits a unique ground-energy state and, therefore, that the E versus S curve for the stable equilibrium states has the shape sketched in Figure 15. Using the language of quantum theory, we may express this conclusion by saying that each ground-energy value is nondegenerate, in the sense that it is realized only by one state.

If the proviso were modified to read: "starting from any state of a system it is always possible to reach either a stable equilibrium state or a ground energy state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process", then the second law would be consistent with the possibility that for a given set of values of amounts of constituents and parameters a system admits more than a single ground-energy state, i.e., consistent with the possibility that a ground-energy value be degenerate, in the sense that it is realized by more than a single state.

Indeed, with the modified statement and for given values of the amounts of constituents and parameters of a system A , we would conclude that the curved boundary of the projection onto the E versus S plane could take the shape shown in Figure 16. Specifically, the horizontal line $E_g A_g$ represents the E versus S relation for all the states that are not stable equilibrium but have the

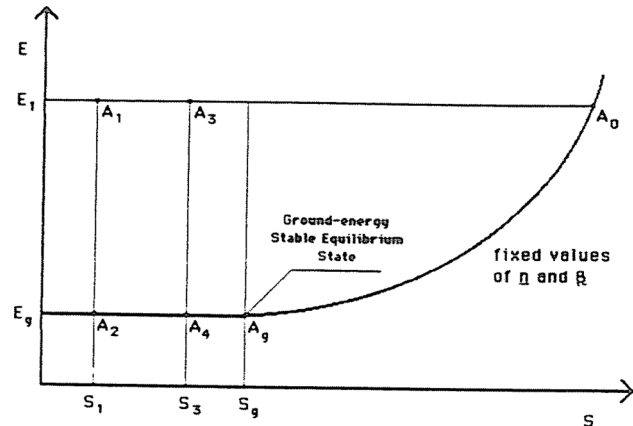


Fig. 16

ground-state energy E_g , and the curve $A_g A_0$ the E versus S relation, for the stable equilibrium states. Each point on the line $E_g A_g$, except A_g , is the projection of states none of which can be stable equilibrium, whereas each point on the curve $A_g A_0$ is a unique stable equilibrium state.

To verify the last assertion, we note that given a set of values of amounts of constituents and parameters for which A_g is the ground-energy stable equilibrium state, a reversible weight process starting from a state A_1 of system A would reach a stable equilibrium state if the entropy of A_1 is greater than or equal to that of A_g , otherwise it would reach a ground-energy state that is not stable equilibrium.

The value S_g of the entropy of the ground-energy stable equilibrium state A_g would be larger than the lowest possible for the states of system A , and could be different for different values of amounts of constituents and parameters. However, in the limit of very large values of amounts of constituents, it turns out that the stable equilibrium states with sufficiently high temperature have entropy that grows linearly with the amounts of constituents, whereas the entropy S_g of the ground-energy stable equilibrium state grows only logarithmically with the amounts of constituents and, therefore, in this limit, the value of S_g can be taken for practical purposes to be negligible, and the modification of the statement of the second law to have negligible practical implications. In many texts on thermodynamics where the treatment is restricted from the outset to the stable equilibrium states of systems with very large values of the amounts of constituents, the conclusion just cited is added as part of the third law by stating that S_g is equal to zero for all values of the amounts of constituents and the parameters.

The graph in Figure 16, however, has a disturbing feature. Starting from any state A_1 with entropy $S_1 < S_g$ and using a reversible weight process, we can reach a ground-energy state A_2 that is not stable equilibrium. The adiabatic availability Ψ_1 is represented by the length $A_1 A_2$. Similarly, starting from any state A_3 with energy $E_3 = E_1$, and entropy $S_1 < S_3 < S_g$, and using a reversible weight process, we can reach a state A_4 that is not stable equilibrium. Now, the adiabatic availability $\Psi_3 = \Psi_1$ and is represented by the length $A_3 A_4$. But state A_1 can evolve spontaneously into A_3 and the increase in entropy $S_3 - S_1$ would be created by irreversibility. Then we would conclude that irreversibility does not affect the values of adiabatic availabilities for states with entropy between zero and S_g , a conclusion that is an exception to our understanding of the adverse effects of irreversibility.

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