

## WHAT IS THE "SECOND LAW" ?

by

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### ABSTRACT

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.

### PREMISE

In a recent thermodynamics text, Truesdell<sup>[1]</sup> identifies several different "second laws". In a review in 1986, the physicist-philosopher Bunge<sup>[2]</sup> compiles a list of about twenty ostensibly inequivalent but equally vague formulations of the "second law". In a manuscript published in 1983, Lindblad<sup>[3]</sup> 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 that 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 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. We begin our discussion with a brief summary of these concepts. Results derived from the laws of the theory are stated without proofs.

## 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 water molecule, 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,<sup>[4]</sup> 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 atoms, such as the H and O atoms, with amounts denoted, respectively, by  $n_1$  and  $n_2$ ; 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 may be different arrangements of internal forces between constituents. For example, if only  $H_2O$  molecules are considered then the only internal force is that between the  $H_2O$  molecules. Again, if  $H_2O$ ,  $H_2$  and  $O_2$  molecules are considered, and the chemical reaction  $H_2 + \frac{1}{2}O_2 = H_2O$  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  $\beta_1$  stands for the first parameter,  $\beta_2$  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 container which encloses the constituents that belong to the system, and separates them from all the others that do not and are outside the enclosure. Again, another parameter could be the potential  $\gamma$  of a uniform gravitational field in which the constituents are immersed, the potential  $\psi$  of an electromagnetic field in which the constituents are floating, or the area  $\mathcal{A}$  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.<sup>[5]</sup> 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.

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 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. For example, the conditions that energy is conserved and entropy cannot be destroyed are time-dependent. Yet, they will be derived without knowledge of the complete equation of motion.

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 elevation 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  $t_2$ . Said more formally, in the course of interactions a system may not be either separable, or uncorrelated, or both from the systems with which it interacts.

## 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 elevation 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 value  $E_0$ , and the expression

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

where  $m$  is the mass of the weight,  $g$  the gravitational constant, and  $z$  the elevation of the weight.

Energy is an **additive** property. Moreover, energy remains constant in time 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 that as time proceeds energy can neither be created nor destroyed, is of great generality and practical importance, and is known as the **principle of energy conservation**.

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  $A_2$ , we derive an extremely important analytical tool that is used in all physics and engineering applications -- the **energy balance equation**. This equation is based on the additivity of property energy and on the principle of energy conservation. 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.,

$$E_2 - E_1 = E_{A\leftarrow} \quad (2)$$

## TYPES OF STATES

Because the number of independent properties of a system is very large even for a system consisting of a single particle with a single degree of freedom, 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 state 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 most striking consequences of the laws of thermodynamics.

### ADIABATIC AVAILABILITY AND AVAILABLE ENERGY

The main consequence of the second law of thermodynamics is that not all states of a system can be changed to a ground state by means of a weight process, i.e., in general, not all the energy above the ground-state energy can be transferred to the weight in a weight process. In particular, the second law asserts that among all the states of a system with given values of the energy, the amounts of constituents and the parameters, there exists one and only one stable equilibrium state. Moreover, 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.<sup>[6]</sup> It also implies that from any stable equilibrium 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 changes.<sup>[7]</sup> A slightly modified version of the law is discussed later.

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  $\psi_1$ , 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 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  $\Omega_1^R$ . 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  $\Omega_1^R$  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 in the next section.

A noteworthy feature of energy, adiabatic availability, and available energy is that these properties are defined for any state of any system, regardless of whether the state is steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium, and regardless of whether the system has many or few degrees of freedom, or whether its size is large or small.

### 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  $S_1$ . Entropy is a property in the same sense as energy is a property. It can be evaluated by means of an auxiliary reservoir R, a reference state  $A_0$  to which is assigned a fixed reference value  $S_0$ , and the expression

$$S_1 = S_0 + c_R^{-1} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)] \quad (3)$$

where  $c_R$  is a well-defined constant -- for the given auxiliary reservoir R -- selected in such a way that the values of entropy found by means of Equation 3 are independent of the reservoir. In other words, despite the dependence of the value  $\Omega_1^R - \Omega_0^R$  in Equation 3 on the selection of the reservoir R, we can show that there is a constant property  $c_R$  of reservoir R that makes the right-hand side of Equation 3 independent of R, so that S is a property of system A only, in the same sense that energy E is a property of system A only. Later on, when temperature is defined as a property of stable equilibrium states, we can show that  $c_R$  equals the constant temperature of reservoir R.

Entropy -- like energy -- is an additive property. Whereas energy remains constant in time whenever the system experiences a zero-net-effect weight process, entropy remains constant in time only when the weight process is reversible. In the course of any irreversible weight process, the system destroys part of its potential ability to transfer energy to a weight, and its entropy increases with time. Because of additivity, and because any process of a system can always be thought of as part of a weight process of an overall system consisting of all the interacting systems, the conclusions that as time proceeds entropy can either be created, if the process is irreversible, or remain constant, if the process is reversible, but can never be destroyed, are of great generality and practical importance, and are known as the **principle of entropy nondecrease**. The entropy created as time proceeds during an irreversible process is called **entropy generated by irreversibility** or **entropy production due to irreversibility**.

Entropy -- like energy -- can be transferred between systems by means of interactions. Denoting by  $SA^{\leftarrow}$  the net amount of entropy 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  $A_2$ , we derive another extremely important analytical tool that -- together with the entropy balance -- is used in all physics and engineering applications -- the **entropy balance** equation. This equation is based on the additivity of property entropy and on the principle of entropy nondecrease. It requires that, as a result of a process, the change in the entropy of the system from  $S_1$  to  $S_2$  must be equal to the net amount of entropy  $SA^{\leftarrow}$  transferred into the system, plus the amount of entropy  $S_{irr}$  generated inside A due to the irreversibility of the process, i.e.,

$$S_2 - S_1 = SA^{\leftarrow} + S_{irr} \quad (4)$$

It is worth repeating that S is defined for any state of any system because E and  $\Omega^R$  are defined for any state of any system.

## 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 [8]

$$P = P(E, n_1, n_2, \dots, n_r, \beta_1, \beta_2, \dots, \beta_s) \quad (5)$$

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 5, when written for property entropy, i.e.,

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

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 partial derivatives of 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,  $n_1, n_2, \dots, n_r$ , in the sense that  $(\partial^2 S / \partial E^2)_{\underline{n}, \underline{\beta}} \leq 0$ , and  $(\partial^2 S / \partial n_i^2)_{E, \underline{n}, \underline{\beta}} \leq 0$  for each i. It is also concave in each of the parameters  $\beta_1, \beta_2, \dots, \beta_s$  which are additive, again in the sense that  $(\partial^2 S / \partial \beta_j^2)_{E, \underline{n}, \underline{\beta}} \leq 0$ . 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 6 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

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

The function  $E(S, \underline{n}, \underline{\beta})$  admits partial derivatives of 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.,

$$T = (\partial S / \partial E)_{\underline{n}, \underline{\beta}}^{-1} = (\partial E / \partial S)_{\underline{n}, \underline{\beta}} \quad (8)$$

The **total potential of the  $i$ -th constituent**  $\mu_i$  is defined by either of the two relations

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

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

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

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

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

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 constituent common in two systems is a necessary condition for the two systems to be in mutual stable equilibrium if that constituent 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.

In terms of  $T$ ,  $p$ ,  $f_j$ 's and  $\mu_i$ 's, the differences in energy,  $dE$ , entropy,  $dS$ , volume,  $dV$ , parameters,  $d\beta_2, \dots, d\beta_s$ , and amounts of constituents,  $dn_1, dn_2, \dots, dn_r$ , between two neighboring stable equilibrium states are related by

$$dE = TdS - pdV + \sum_{j=2}^s f_j d\beta_j + \sum_{i=1}^r \mu_i dn_i \quad (12)$$

## WORK AND HEAT 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  $E_{A \leftarrow}$  equals the negative of the work done on the environment  $W_{A \rightarrow}$ , i.e.,  $E_{A \leftarrow} = -W_{A \rightarrow}$ , and the entropy exchange  $S_{A \leftarrow} = 0$ . Therefore, the energy and entropy balances are

$$E_2 - E_1 = -W_{A \rightarrow} \quad (13)$$

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

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  $E_{A \leftarrow} = Q_{A \leftarrow}$ , and the entropy exchange  $S_{A \leftarrow} = Q_{A \leftarrow} / T_Q$ . Therefore, the energy and entropy balances are

$$E_2 - E_1 = Q_{A \leftarrow} \quad (15)$$

$$S_2 - S_1 = Q_{A \leftarrow} / T_Q + S_{irr} \quad (16)$$

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

$$E_2 - E_1 = Q_{A \leftarrow} - W_{A \rightarrow} \quad (17)$$

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

or, for differential changes,

$$dE = \delta Q_{A \leftarrow} - \delta W_{A \rightarrow} \quad (19)$$

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

Equations 19 and 20 can be combined with Equation 12 to find relations between interaction transfers of energy and entropy and changes in properties.

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

Other interactions, involving transfers of energy, entropy, and amounts of constituents, can be defined but will not be discussed here.

### 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 vertical line denoted as the line of the zero-entropy states, and the curve of the stable equilibrium states.

A point either inside the cross-hatched area or on the vertical line  $S = 0$  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.

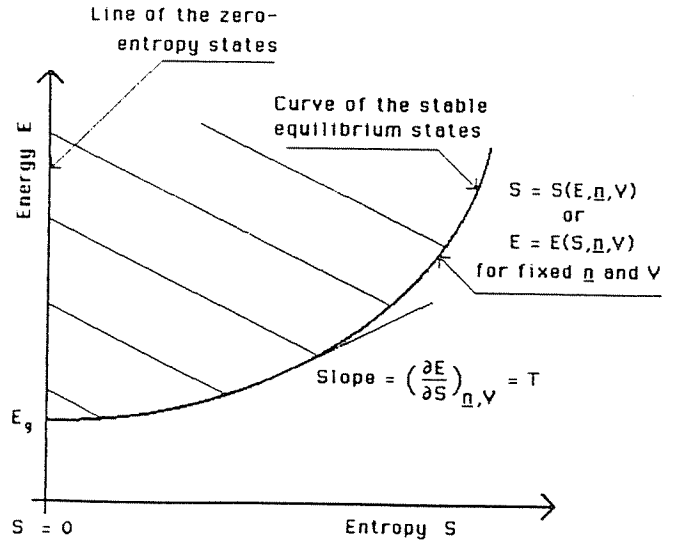


Figure 1

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 the laws of thermodynamics imply that 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. We discuss this conclusion in more detail in the section on the third law.

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 would clearly

differ from  $E_g$ . For other values of the amounts of the constituents and the volume, the lowest energy state is 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  $E$ ,  $\Omega$ , 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 derived from the laws of thermodynamics, and that we summarize below with reference to Figure 2.

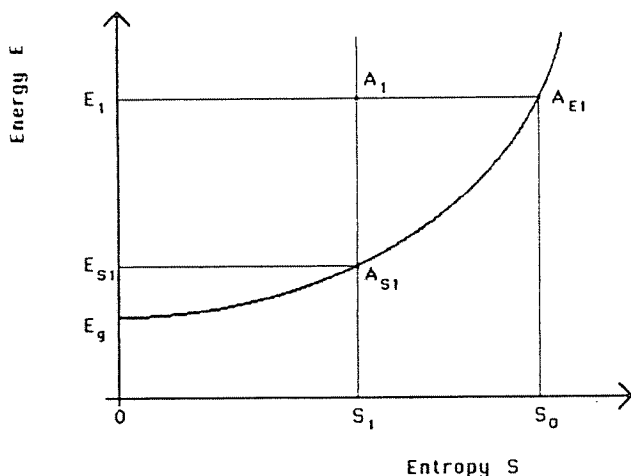


Figure 2

Each stable equilibrium state is a state of lowest energy among all the states with the same values of  $S$ ,  $\Omega$ , and  $V$ . For each set of values  $S_1$ ,  $\Omega$ , and  $V$ , the stable equilibrium state  $A_{S_1}$  on the vertical line  $S = S_1$  is the state of lowest energy -- no states exist below  $A_{S_1}$  that correspond to the same values of  $\Omega$  and  $V$ , and that lie on the line  $S = S_1$ . State  $A_{S_1}$  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  $\Omega$  and  $V$ . Indeed, in such a process the net change in the entropy of the system is zero,  $S_{S_1} = S_1$ , and the energy  $E_1 - E_{S_1}$  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  $E$ ,  $n$ , and  $V$ . For each set of values  $E_1$ ,  $\Omega$ , and  $V$ , the stable equilibrium state  $A_{E_1}$  on the horizontal line  $E = E_1$  is the state of highest entropy -- no states exist beyond  $A_{E_1}$  that correspond to the same values of  $\Omega$  and  $V$  and that lie on the line  $E = E_1$ . In an isolated system -- a system experiencing no interactions -- state  $A_{E_1}$  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  $(\partial E / \partial S)_{\Omega, V}$  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  $S$ ,  $\Omega$ , 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  $S$ ,  $\Omega$ , 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 be measurable by the techniques of temperature measurements.

### Perpetual Motion of the Second Kind

Starting from a stable equilibrium state  $A_{S_1}$  on the convex boundary  $E_g A_{S_1} A_{E_1}$ , 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  $A_{S_1}$ . Indeed, if energy were transferred to a weight, the energy of the system would be reduced. But starting from state  $A_{S_1}$  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 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  $\Omega$  and  $V$ .

### Classical Thermodynamics

For each set of given values of amounts of constituents and volume, the convex boundary  $E_g A_{S_1} A_{E_1}$  represents the corresponding stable equilibrium states. These are the states considered in equilibrium thermodynamics, which is sometimes also called "classical thermodynamics" or "thermostatistics". These



states are often referred to in the literature as the thermodynamic equilibrium states. So, equilibrium 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  $E_1 - E_{S_1}$  shown graphically in Figure 3 is equal to the adiabatic availability  $\psi_1$  of  $A_1$  because the change of state from  $A_1$  to  $A_{S_1}$  represents the change specified in the definition of  $\psi_1$ . We see from the figure that, in general,  $\psi_1$  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  $E_1$ ,  $\Omega$  and  $V$ . So entropy affects the usefulness of the energy of a system, i.e., the larger the entropy for given values of  $E$ ,  $\Omega$  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  $\Omega$  and  $V$  is a consequence of the laws of thermodynamics of paramount theoretical importance and with many practical implications.

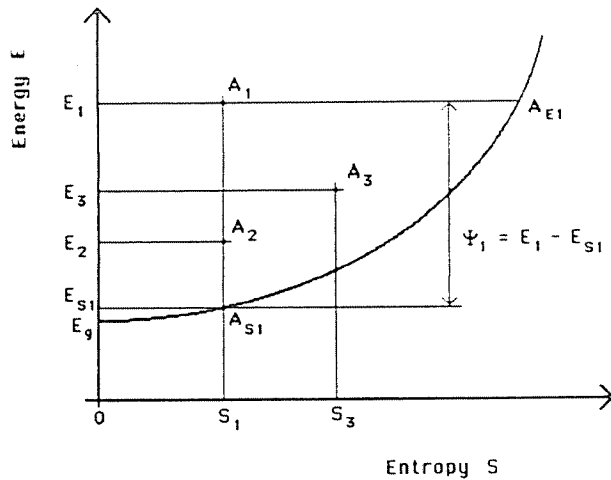


Figure 3

For given values of  $\Omega$  and  $V$ , we see graphically from Figure 3 that stable equilibrium states, such as for example state  $A_{S_1}$ , 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  $A_{S_1}$  (Figure 3) is always smaller than the adiabatic availability  $\psi_1$ .

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

$$(WA)_{rev} = E_1 - E_2 < E_1 - E_{S_1} = \psi_1 \quad (21)$$

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

$$(WA)_{irr} = E_1 - E_3 < E_1 - E_{S_1} = \psi_1 \quad (22)$$

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.

### Available Energy

The  $E^R$  versus  $S^R$  diagram of a reservoir  $R$  is just a straight line of slope  $T_R$  (Figure 4) because the reservoir passes through stable equilibrium states only, and can be shown to have 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.

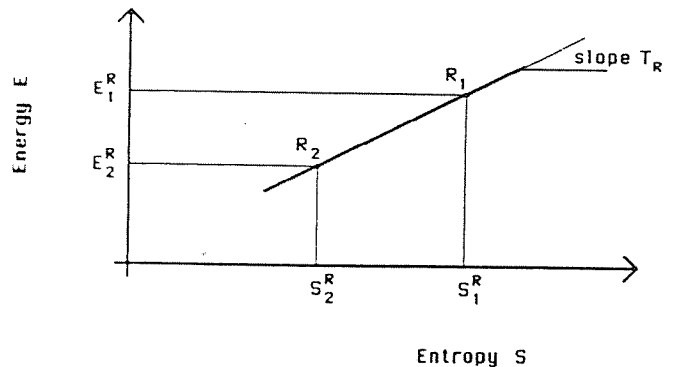


Figure 4

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  $T_R$ , 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  $E_g A_{S_1} A_0$  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  $T_0 = (\partial E / \partial S)_{B,V}$  and, therefore, equal to the temperature  $T_R$  of the reservoir. In state  $A_0$  the system has energy  $E_0$  and entropy  $S_0$

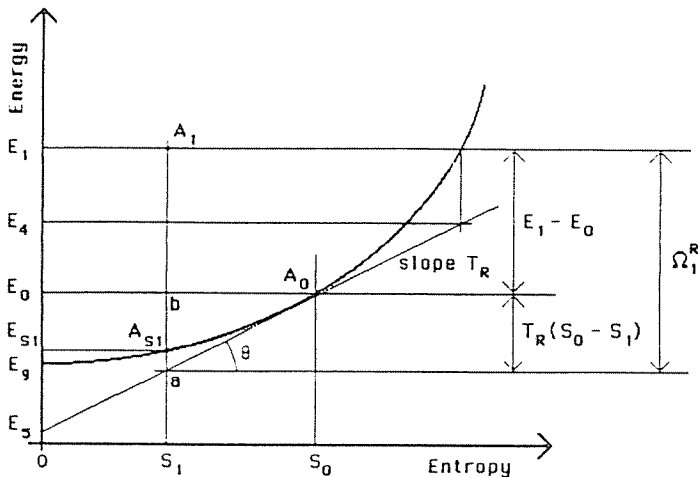


Figure 5

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  $\Omega_1^R$  of  $A_1$  with respect to reservoir R.

Indeed, with respect to reservoir R, the available energy  $\Omega_1^R$  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  $\Omega_0^R$  of state  $A_0$  is zero. We recall that the available energy  $\Omega_1^R$  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 4).

The term  $E_1 - E_0$  in the right-hand side of Equation 23 is the length  $bA_1$  in Figure 5, 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 4). 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  $\Omega_1^R$  of state  $A_1$ .

The graphs in Figures 4 and 5 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  $\psi_1$  and  $\Omega_1^R$  (Figures 3 and 5), we see that in general the available energy  $\Omega_1^R$  is greater than the adiabatic availability  $\psi_1$ . We also see that  $\Omega_1^R$  can be greater than the energy of the system above the ground-state energy,  $E_1 - E_0$ . For states with energy  $E_1$ , the available energy varies from the largest value  $E_1 - E_5$  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 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 5) is as follows. We first use machinery that interacts reversibly and adiabatically with A only, and extracts the adiabatic availability  $\psi_1$ . Thus, system A is brought to stable equilibrium state  $A_{S_1}$ . 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 cool or heat the system to temperature  $T_R$  while producing work. Thus, the total work done  $\Omega_1^R$  is greater than  $\psi_1$ .

### Examples of Work Interactions

Graphical illustrations of work-only interactions between two systems A and B are provided by Figure 6. 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 A and B are zero because a work interaction does not transfer any entropy and the processes for both A and B are reversible.

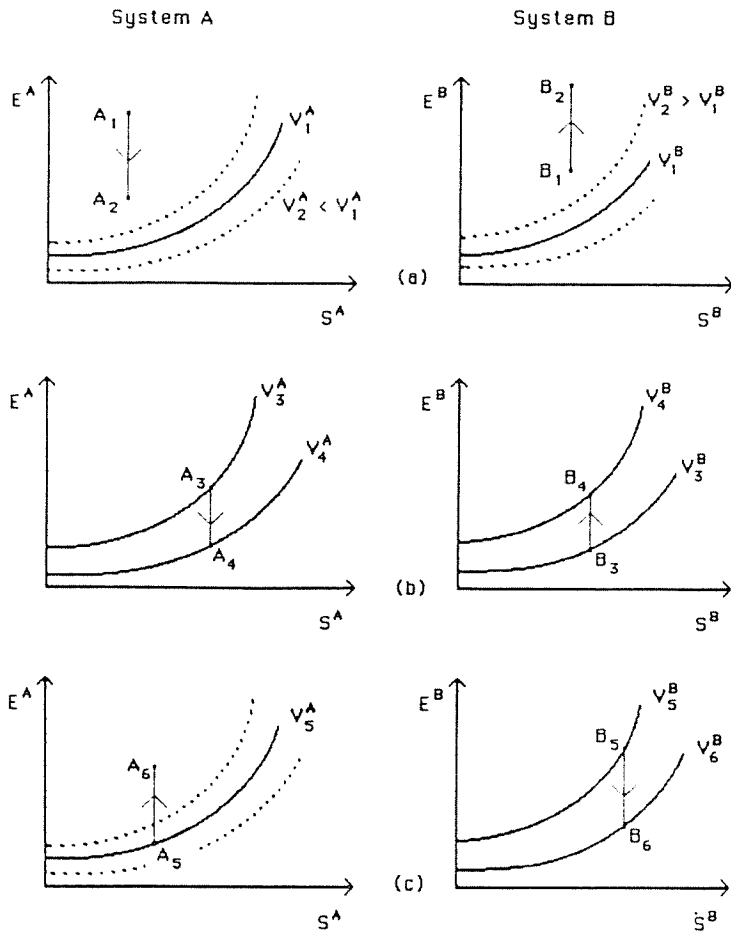


Figure 6

As a result of the interaction depicted in Figure 6a, 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 6b, 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 6c, 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 6a and 6c, 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 6a, 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 6c, 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 6b 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 7 and 8. 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.

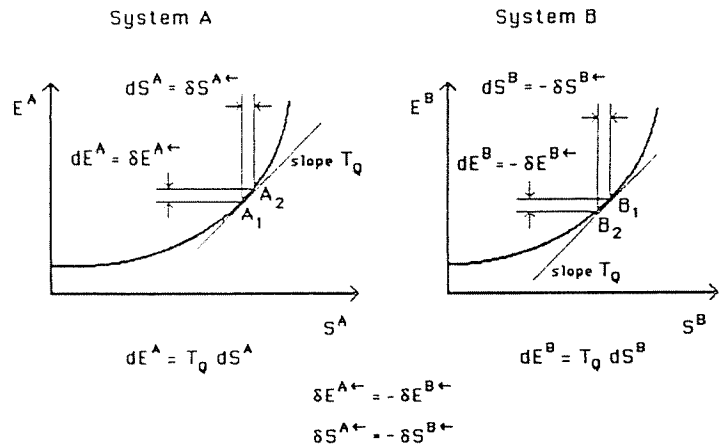


Figure 7

As a result of the heat interaction shown in Figure 7, 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 8, 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 contain subsystems  $A'$  and  $B'$ , respectively, which change from stable equilibrium states  $A'_1$  and  $B'_1$  to stable equilibrium states  $A'_2$  and  $B'_2$ , all with temperatures almost equal to  $T_0$ . Thus, the interaction between subsystems  $A'$  and  $B'$  is of the same kind as that sketched in Figure 7. 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.

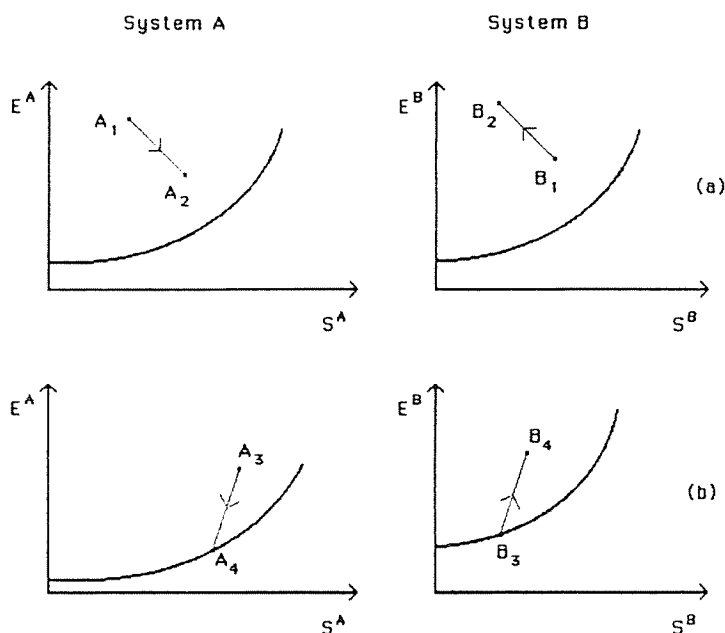
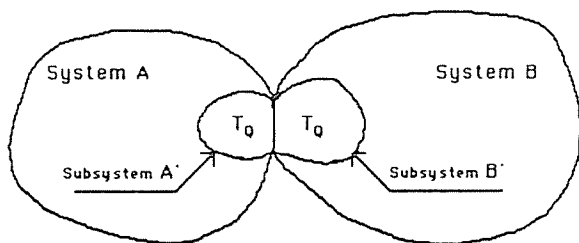


Figure 9

As a result of the interaction shown in Figure 9a, 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 7 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 8 because the ratio of the energy exchanged to the entropy exchanged is negative.

As a result of the interaction shown in Figure 9b, the energy and the entropy of system A are both decreased as A changes from nonequilibrium 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 nonequilibrium 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 interaction cannot be heat in the strict sense illustrated in Figure 7. It is not heat even in the generalized sense represented in Figure 8 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.

All the processes represented in Figure 9 could evolve into irreversible processes. For example, in Figure 9a, irreversibility could occur in either system A, or

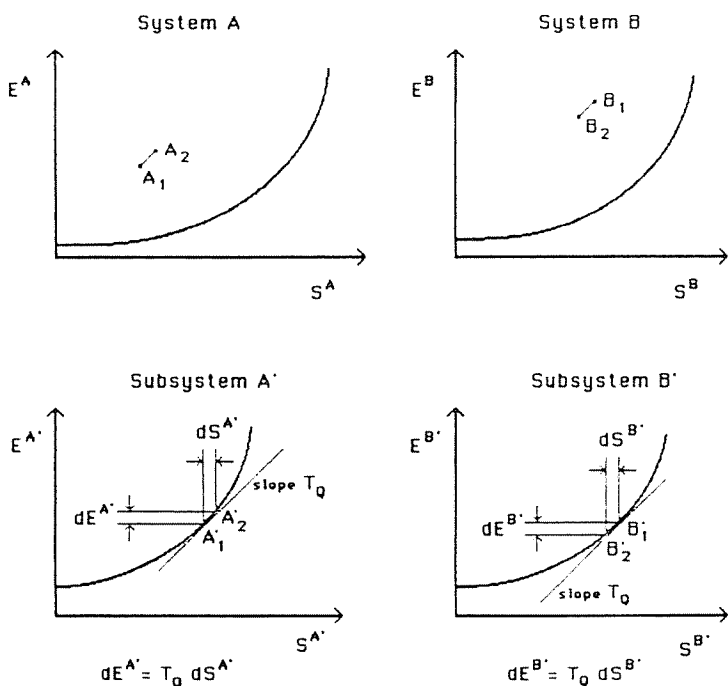


Figure 8

### Examples of Other Nonwork Interactions

Nonwork interactions that are not heat between two systems A and B are illustrated in Figure 9 where the combination of A and B is isolated and all processes are assumed to be reversible.

system B, or both because the final states of both A and B are not stable equilibrium.

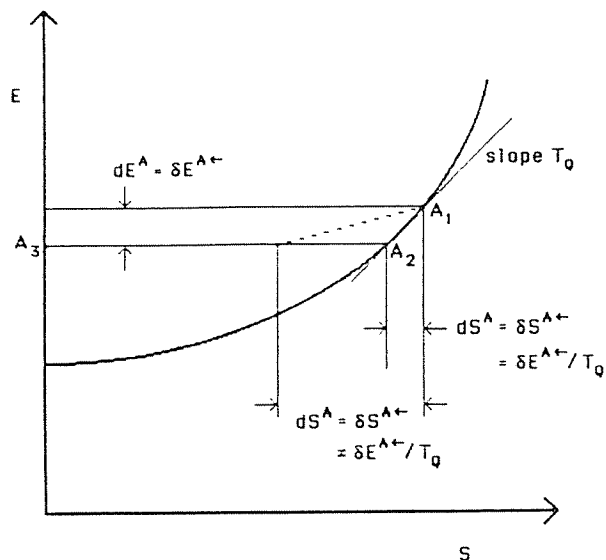


Figure 10

The need for the distinction between heat and other types of nonwork interactions is illustrated by the changes of state shown in Figure 10. System A is initially in a stable equilibrium state  $A_1$  at temperature  $T_0$ . 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  $\delta E^{A\leftarrow}/T_0$ . Therefore, either we call heat all the interactions that involve an exchange of both energy and entropy, but then we cannot use the relation  $\delta E^{A\leftarrow} = \delta Q^{A\leftarrow} = T_0 \delta S^{A\leftarrow}$  for all these interactions, or we reserve the term heat for interactions for which  $\delta Q^{A\leftarrow} = T_0 \delta S^{A\leftarrow}$ , 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.

### THE THIRD LAW

We recall that the second law has been 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.

With this proviso, the second law results in the conclusions that: (1) among all the stable equilibrium states with given values of the amounts of constituents  $\underline{n}$  and the parameters  $\underline{\beta}$ , the ground-energy (lowest-energy) stable equilibrium state has the lowest entropy and the lowest temperature; (2) the value  $S_g$  of this lowest entropy is the same for all values of  $\underline{n}$  and  $\underline{\beta}$  of a system and, hence, it is the same for all ground-energy states of all systems; and (3) no other state of the system has entropy lower than  $S_g$ . Because it is common to all the ground-energy states of all systems, we can assign to  $S_g$  the value zero, i.e.,

$$S_g = 0 \quad \text{for all values of } \underline{n} \text{ and } \underline{\beta} \quad (24)$$

It is noteworthy that, in mechanics, each ground-energy state is stable equilibrium, and all mechanical states can be interconnected by means of reversible weight processes. It follows that all the states contemplated in mechanics have the same entropy as that of the ground-energy states, i.e., it follows that mechanics is the physics of zero-entropy states.

The statement of the second law implies that the temperature  $T_g$  of a ground-energy stable equilibrium states is lowest for the given values of  $\underline{n}$  and  $\underline{\beta}$ , but the value of  $T_g$  remains unspecified. To resolve this question without resorting to the formalism of quantum theory, the third law asserts that for each given set of values of the amounts of constituents and the parameters, the lowest-energy stable equilibrium state has zero temperature.

Within the mathematical framework of quantum theory, the third law assertion just stated follows as a theorem of the explicit expression of the stable equilibrium states obtained by applying the highest entropy principle to the explicit expressions of the energy, the amounts of constituents, and the entropy. For example, when the stable-equilibrium energy is given by the well-known canonical formula

$$E(\underline{n}, \underline{\beta}) = \frac{\text{Tr} H(\underline{n}, \underline{\beta}) e^{-H(\underline{n}, \underline{\beta})/kT}}{\text{Tr} e^{-H(\underline{n}, \underline{\beta})/kT}} \quad (25)$$

then for any set of values  $\underline{n}$  of the amounts and  $\underline{\beta}$  of the parameters the lowest-energy stable equilibrium state has temperature equal to zero, i.e.,  $T_g(\underline{n}, \underline{\beta}) = 0$ . The same follows from the well-known grand-canonical formula.

However, the quantum theoretical formalism also implies that, in general, the value of the entropy of the lowest-energy stable equilibrium state is given by  $S_g(\underline{n}, \underline{\beta}) = k \ln D_g(\underline{n}, \underline{\beta})$  where  $D_g(\underline{n}, \underline{\beta})$  is sometimes called the degeneracy of the lowest-energy value for the given values of  $\underline{n}$  and  $\underline{\beta}$ . With the proviso recalled at the beginning of this section, the second law implies Relation 24 and, therefore, requires that for any system every lowest-energy value be nondegenerate, i.e., that

$$D_g(\underline{n}, \underline{\beta}) = 1 \quad \text{for all values of } \underline{n} \text{ and } \underline{\beta} \quad (26)$$

Many authors<sup>[9]</sup> have argued that Condition 26 is too restrictive because there are systems in nature for which the entropy of the lowest-energy stable equilibrium state is nonzero and a function of  $\underline{n}$  and  $\underline{\beta}$ , i.e.,  $D_g(\underline{n}, \underline{\beta}) > 1$ .

To account for the existence of such systems, the proviso in the second law should be 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. The third law as stated above would remain unmodified and still imply that each ground-energy stable equilibrium state has zero temperature.

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 11, rather than the shape shown in Figure 1. 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 ground-state energy  $E_g$ , and the curve  $A_g A_{E1}$  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  $A_g A_{E1}$  is a unique stable equilibrium state.

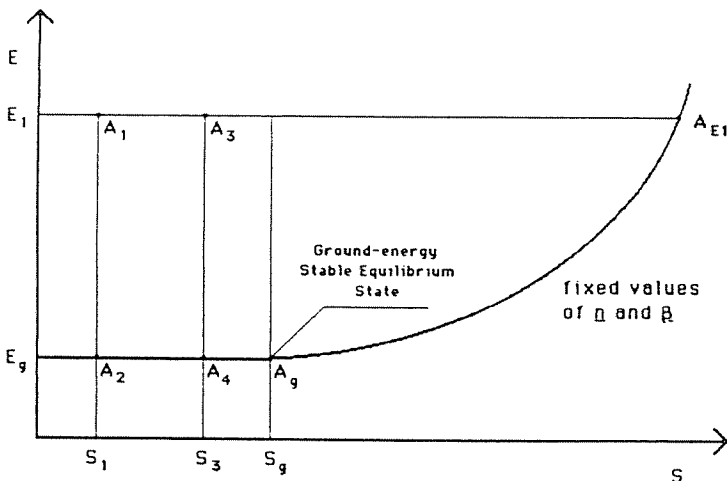


Figure 11

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. Not being stable equilibrium, none of the states with  $E = E_g$  and  $0 \leq S < S_g$  can be assigned a temperature.

Whether Condition 26 is satisfied by all systems or not, i.e., whether the modified statement of the second law must be adopted or not, can only be decided experimentally on systems in stable equilibrium states at very low temperatures and with very small values of the amounts of constituents. Indeed, for large values of the amounts of constituents, it turns out that even at relatively low temperatures the stable equilibrium states have entropy that grows linearly with the amounts of constituents, whereas the entropy  $S_g$  of the ground-energy stable equilibrium states -- if not zero -- would grow only logarithmically with the amounts of constituents. Under such conditions, the value of  $S_g$  would give a negligible contribution to the entropy and, hence, could hardly be detected. For systems for which the foregoing comment applies, the modified proviso in the second law would have nonnegligible practical implications only for very low-temperatures and very-few-particle states.

The modified proviso, would also result in an interesting exception to our general understanding of irreversibility. 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 (Figure 11). The adiabatic availability  $\psi_1$  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 general understanding of the adverse effects of irreversibility.

#### REFERENCES AND FOOTNOTES

1. C. Truesdell, Rational Thermodynamics, Springer-Verlag, New York, 1984.
2. M. Bunge, Philosophy of Science, Vol. 53, 305 (1986).
3. G. Lindblad, Nonequilibrium Entropy and Irreversibility, Reidel, Dordrecht, Holland, 1983.
4. Formally, a system is well-defined only if it is separable and uncorrelated from any other physical object in its surroundings.

5. The term value is used in the sense of quantum physics, i.e., a mean value of repeated measurement results performed on a homogeneous ensemble (see J. von Neumann, Mathematical Foundations of Quantum Mechanics, Princeton University Press, 1955).

6. This statement of the second law is an outgrowth of the work of J.M. Reenan, G.N. Hatsopoulos, and E.P. Gyftopoulos. See the article "Principles of Thermodynamics," Macropedia, Encyclopaedia Britannica. All other correct statements of the second law can be shown to be special cases of the statement given here.

7. For brevity, the discussion in this article is restricted to systems with no upper bounds in the value of the energy.

8. For brevity, we do not discuss the form of Equation 5 for a system with internal reaction mechanisms between constituents, such as chemical or nuclear reactions.

9. See, for example, H.B.G. Casimir, Z. Physik, Vol. 171, 246 (1963); H.J. Klein, Rendiconti S.I.E., 10th Course, 1 (1960); R.B. Griffiths, in A Critical Review of Thermodynamics, Eds. E.B. Stuart, B. Gal-Or, and A.J. Brainard, Mono Book Co., Baltimore, 1970.