What is Heat?*

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We define heat as a particular kind of nonwork interaction that involves only energy and entropy transfers, and that is entirely distinguishable from work. The existence of heat interactions is a consequence of the first and second laws of thermodynamics. The requirement that heat be entirely distinguishable from work implies strict conditions on the end states of the interacting systems, and guarantees a definite relation between such states and the energy and entropy transfers. We illustrate these conditions by using energy versus entropy graphs. Many experiences can be represented as heat interactions, including the exchanges between two black bodies at temperatures that differ infinitesimally. We discuss the latter point in a companion paper at this conference. [DOI: 10.1115/1.4026382]

1 Introduction

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

For example, in his lectures on physics, Feynman [1] describes heat as one of several different forms of energy related to the jiggling motion of particles stuck together and tagging along with each other (pp. 1–3 and 4–2), a form of energy which really is just kinetic energy—internal motion (p. 4–6), and is measured by the random motions of the atoms (p. 10–8). Tisza [2] argues that such slogans as "heat is motion," in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value.

There are at least two problems with these illustrations. First, work and heat are not stored in a system. Each is a mode of transfer of energy from one system to another. Second, and perhaps more important, concepts of mechanics are used to justify and make plausible a notion—that of heat—which is beyond the realm of mechanics. In spite of these logical drawbacks, the trick works because at first the student finds the idea of heat harmless, even natural. But the situation changes drastically as soon as the notion of heat is used to define a host of new ideas, less natural and less harmless. At once, heat is raised to the same dignity as work, it is contrasted to work and used as an essential ingredient in the first law. The student begins to worry because the notion of heat is less definite than and not as operational as that of work.

The first problem is addressed in some expositions. Landau and Lifshitz [3] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim [4] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [5] defines heat as that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. Similar definitions are adopted in notable textbooks, such as Van Wylen and Sonntag [6], Wark [7], Huang [8], Modell and Reid [9], and Moran and Shapiro [10].

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

In our experience, whenever heat is introduced before the first law, and then used in the statement of the second law and in the definition of entropy, the student cannot avoid but sense ambiguity and lack of logical consistency. This results in the wrong but unfortunately widely spread conviction that thermodynamics is a confusing, ambiguous, hand-waving subject.

During the past twenty years of teaching thermodynamics to students from all over the globe, we have sensed a need for more clarity, unambiguity and logical consistency in the exposition of thermodynamics than provided by traditional approaches. Continuing the effort pioneered by Keenan and Hatsopoulos, we have composed an exposition [12] in which we strive to develop the basic concepts without ambiguities and logical inconsistencies, building upon the student's sophomore background in introductory physics.

The basic concepts and principles are introduced in a novel sequence that eliminates the problem of incomplete definitions, and that is valid for both macroscopic and microscopic systems, and for both equilibrium and nonequilibrium states. The laws of thermodynamics are presented as fundamental laws of physics that complement the laws of dynamics. Heat plays no role in the first law, the definition of energy, the second law, the definition of entropy, and the concepts of energy and entropy exchanges between interacting systems. It emerges as a consequence of these concepts and laws. For convenience, we summarize this exposition in the Appendix.

Heat is the energy exchanged between systems that interact under very restrictive conditions that define what we call a heat interaction. In this paper we discuss the definition of a heat interaction [13], and illustrate its effects on the interacting systems by means of energy versus entropy graphs.

2 Interactions

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

In addition, if as a result of interactions a system is brought to a state that is not stable equilibrium, this state may evolve spontaneously towards equilibrium thus causing further changes in the values of the properties of the system. For example, the spontaneous evolution of a nonequilibrium state towards equilibrium causes a spontaneous creation of entropy within the system, i.e., such

*Proceedings of the Winter Annual Meeting of the American Society of Mechanical Engineers, Dallas, TX, November 25–30, 1990, in Education in Thermodynamics and Energy Systems, edited by G. Tsatsaronis, M. J. Moran, and A. Bejan, ASME book G00567, AES-Vol. 20, pp. 33–41 (1990). Reprinted with permission.

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evolution is irreversible. Thus, interactions may cause a change in entropy of a system either directly by inducing an exchange of entropy through its boundary, or indirectly by inducing an irreversible spontaneous change of state, or both.

Knowing how much of the change of a property is due to exchanges with other systems and how much to spontaneous creation or destruction within the system is very important to the understanding of the performance of the system. For example, if the entropy of a system A increases only because of entropy transfers from other systems, then such an increase implies no imperfections within A and no opportunities for improvements by modifications of A. On the other hand, if the same entropy increase is due solely to irreversibility within A, then this increase implies imperfections within A, and is subject to reduction by proper redesign of A.

A practical method of identifying the system in which entropy is generated in the course of interactions is by specifying each interaction in terms of the net exchanges that it causes at the boundary between the interacting systems. For this reason, interactions are classified into different categories depending on whether the interacting systems exchange, for example, energy but no constituents and no entropy, or energy and entropy but no constituents, or energy, entropy, and constituents.

The simplest illustration of these ideas is afforded by an interaction between two identical systems A and B, in states A_1, A_2, B_1 and B_2 with identical values of the amounts of constituents and the parameters. Thus, the stable-equilibrium-state curve of A is identical to that of B, and we can represent the end states of both systems on a single energy versus entropy graph. Such a graph is shown in Fig. 1. States A_1 and A_2 have the same value of the entropy, i.e., $S_2^A - S_1^A = 0$, and so the entropy balance for system A, $S_2^A - S_1^A = -S^{A\rightarrow} + S_{\text{irr}}^A$, yields $S^{A\rightarrow} = S_{\text{irr}}^A \geq 0$, where $S^{A\rightarrow}$ is the entropy transferred out of A, and S_{irr}^A the entropy generated by irreversibility in A. The energy balance is $E_2^A - E_1^A = -E^{A\rightarrow}$, where $E^{A\rightarrow}$ is the energy transferred out of A. Similarly, for system B states B_1 and B_2 have the same entropy, $S_2^B - S_1^B = 0$, and the entropy balance, $S_2^B - S_1^B = S^{B\leftarrow} + S_{\text{irr}}^B$, yields $S^{B\leftarrow} = -S_{\text{irr}}^B \leq 0$, The energy balance is $E_2^B - E_1^B = -E^{B\rightarrow}$.

If systems A and B interact only with each other and not with any other systems, the composite system AB does not experience any exchange with any other system and so $E^{AB\leftarrow}$ 0 and $S^{AB\leftarrow} = 0$. For the given states of systems A and B, the energy balance for the composite AB, $E_2^A - E_1^A + E_2^B - E_1^B = E^{AB\leftarrow} = 0$, yields $E^{B\rightarrow} = E^{A\leftarrow}$, and the entropy balance, $S_2^A - S_1^A + S_2^B - S_1^B = S^{AB\leftarrow} + S_{\text{irr}}^{AB} = 0$, yield $S_{\text{irr}}^{AB} = S_{\text{irr}}^B + S_{\text{irr}}^B = 0$ or $S_{\text{irr}}^A = S_{\text{irr}}^B = 0$ and $S^{A\rightarrow} = S^{B\leftarrow} = 0$. We conclude that the exchange of energy between the two systems is not accompanied by any exchange of entropy, and we say that the two systems experience a work interaction. We call work and denote with the symbol $W^{A\rightarrow B}$ the amount of energy exchanged, i.e. $W^{A\rightarrow B} = E^{A\rightarrow} = E^{B\leftarrow}$. Graphically, the work is represented by the length of the vertical segment A_1A_2 or the vertical segment B_1B_2 on the graph in Figure 1.

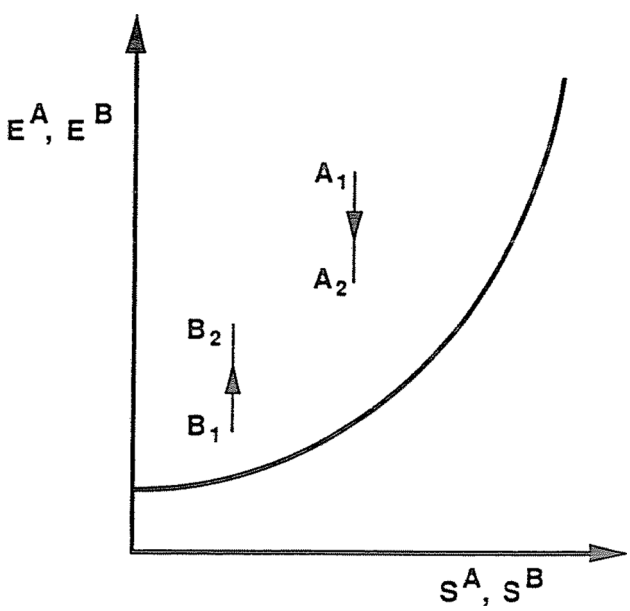
If as a result of an interaction a system is brought to a state that is not stable equilibrium, this state may evolve spontaneously towards equilibrium thus causing further changes in the values of the properties of the system. For example, spontaneous evolutions of nonequilibrium states A_2 and B_2, towards stable equilibrium states A_3 and B_3, respectively, are shown in Figure 2. Each spontaneous evolution is irreversible and causes a generation of entropy within the system. As system A evolves from state A_2 to state A_3 spontaneously, i.e., without experiencing any exchange with any other system, the amount of entropy generated by irreversibility $S_{\text{irr}}^A = S_3^A - S_2^A$. This entropy generation is represented graphically by the length of the horizontal segment A_2A_3. Similarly, for system B, $S_{\text{irr}}^B = S_3^B - S_2^B$ and is represented graphically by the length of the horizontal segment B_2B_3.

The foregoing example shows that a work interaction is not accompanied by any exchange of entropy between the interacting systems, but it can cause the generation of entropy by irreversibility by placing at least one of the interacting systems in a nonequilibrium state, because such a state can change spontaneously and irreversibly towards stable equilibrium.

3 Processes

The notion of a process is introduced in thermodynamics to bypass the lack of a complete equation of motion for all phenomena. It is defined as the combination of three key features that characterize a time evolution of a system: (1) the initial state, i.e., the state at the time t_1; (2) the final state, i.e., the state at a subsequent time t_2; and (3) the type of interaction experienced by the system as it goes from the initial to the final state, i.e., during the time interval between t_1 and t_2.

A system may experience the same change of state in many different ways. For example, the change of state from A_1 to A_3 sketched in Figure 2 may occur either as a result of a work



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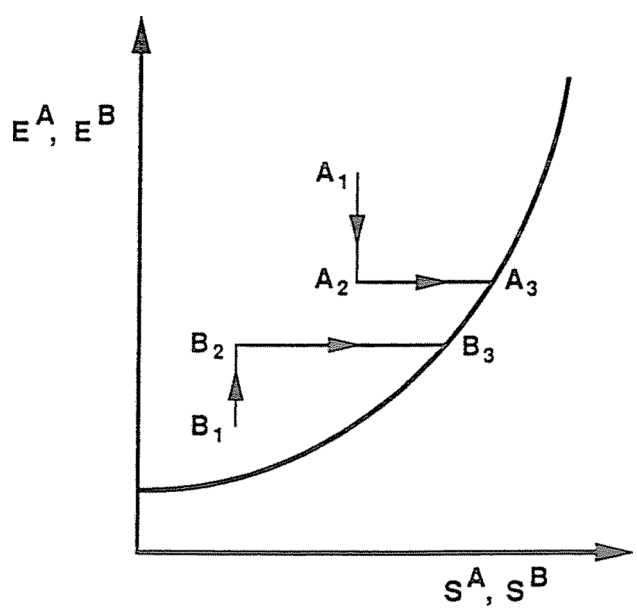

Fig. 2 See text

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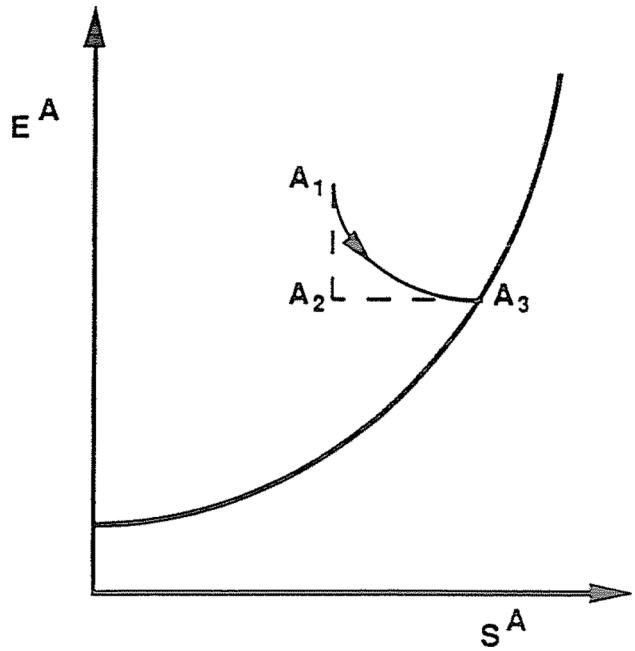

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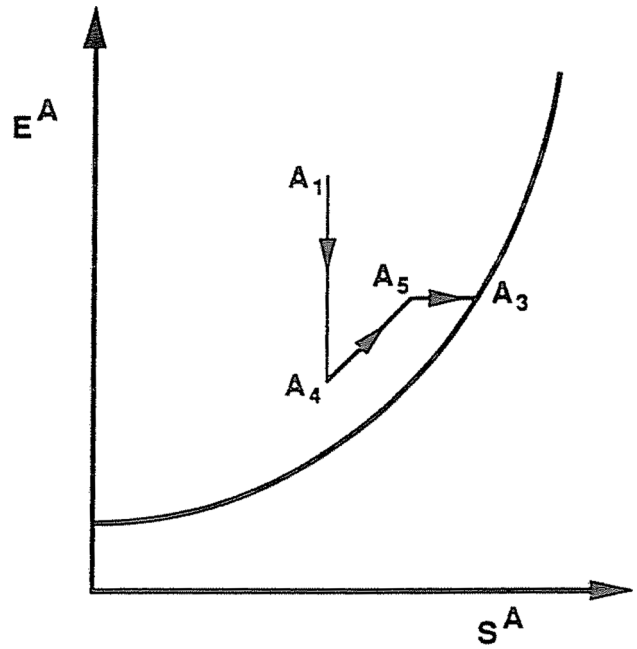


Fig. 4 See text

interaction with system B followed by a spontaneous evolution of the state of A toward equilibrium, or as a result of a simultaneous work interaction and a spontaneous evolution toward equilibrium as represented by the curved path A_1A_3 in Figure 3.

To make ideas specific, we take A to be a battery, charged in state A_1 at time t_1, and B a weight attached to the shaft of a perfect motor. Between t_1 and t_2 the motor is connected via cables to the battery. The battery ends in state A_2, and the weight is raised. Between t_2 and t_3 the battery is perfectly isolated and discharges internally until it reaches state A_3.

Clearly, the mechanisms that cause the internal discharge are always active. If the rate of the internal discharge is much slower that the rate of the work interaction with the weight, the sequence of states is as sketched in Fig. 2. If the rate of the internal discharge and the rate of the work interaction with the weight are comparable the states from A_1 to A_3 follow a path somewhat similar to that shown in Fig. 3.

By definition, the two processes from A_1 to A_3 are identical even though they involve different sequences of states and, hence, different paths on the energy versus entropy graph. They are identical because they consist of the same initial and final states, and the same type of interaction, here a work interaction.

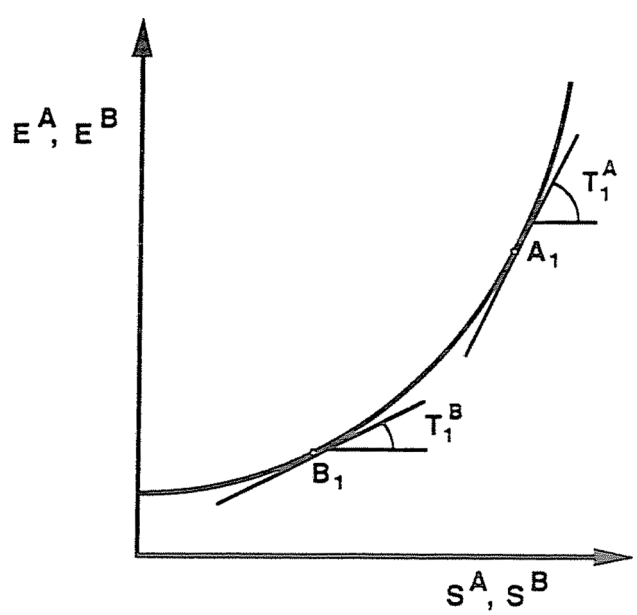
A given change of state from A_1 to A_3 can be achieved by a variety of different processes some of which may involve entropy exchanges between system A and its environment. A sequence of states that result from a fast work interaction (A_1 to A_4) followed by a fast nonwork interaction (A_4 to A_5) and a subsequent slow spontaneous evolution of the state of A toward equilibrium (A_5 to A_3) is shown in Figure 4. For example, the battery A powers the motor between t_1 and t_4, and ends in a state A_4 with lower energy than the state A_2 considered earlier. Then, between t_4 and t_5, the battery receives energy and entropy from another system C, and ends in state A_5. Finally, between t_5 and t_3 the battery is perfectly isolated and discharges internally until it reaches state A_3.

Energy and entropy balances are used to evaluate the performance of a system during a given time interval. To this end, the notion of a process and, therefore, the characterization of each type of interaction must provide a unique unambiguous way to account for the amounts of energy and entropy exchanged by the system during the given time interval. This requirement can be met only by precise and restrictive definitions of different kinds of interaction. For example, we have seen that a work interaction is defined by the very restrictive requirement that no entropy be exchanged.

4 Heat Interactions

As we suggest in Sec. 1 heat is not a primitive concept. Its definition requires the concepts of energy, entropy, energy and entropy exchange, stable equilibrium state, and temperature.

Even if introduced after the definitions of all these concepts, the statement that heat is an exchange of energy that differs from work and is determined by a temperature difference is insufficient to specify a definite and unambiguous relation between the energy and the entropy exchanges. To see this clearly we consider two identical systems A and B with identical values of amounts of constituents and parameters, and their coincident energy versus



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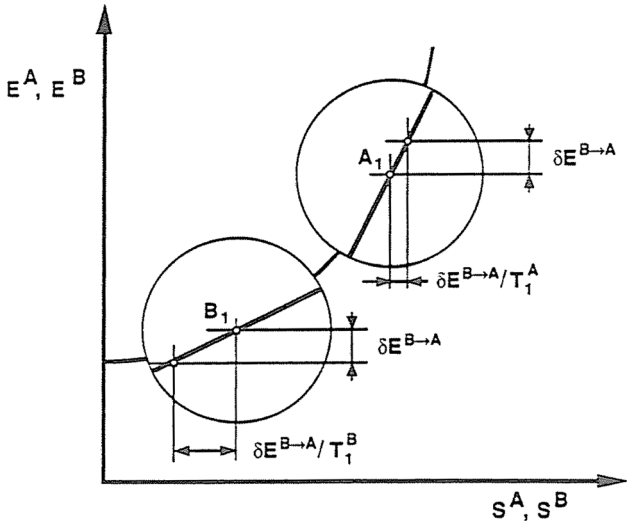

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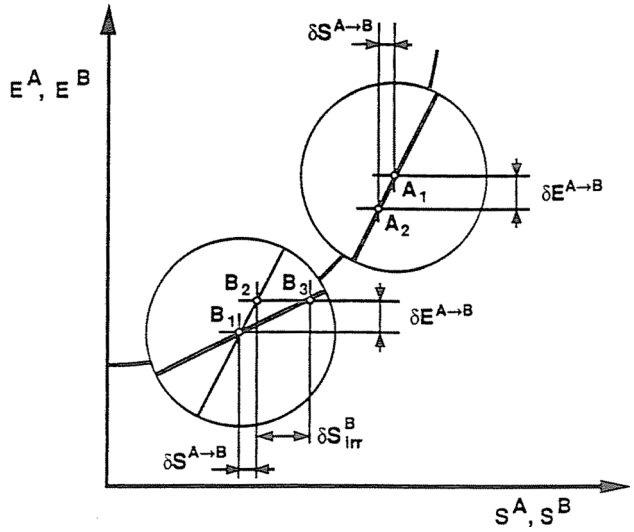

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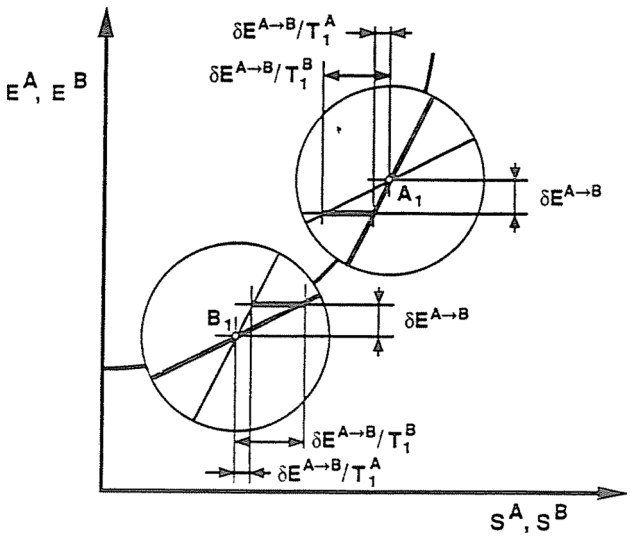

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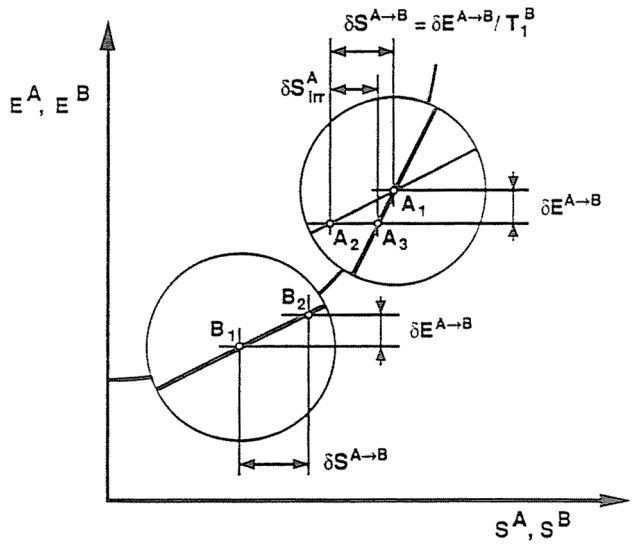

Fig. 9 See text

entropy graphs (Figure 5). The initial state of A is A_1 at temperature T_1^A, and the initial state of B is B_1 at temperature T_1^B.

Within the set of all the stable equilibrium states of a system, the laws of thermodynamics imply that energy, entropy, amounts of contituents and parameters cannot be varied independently but are interrelated by a single-valued relation $S = S(E, n, \beta)$. Temperature is the inverse of the partial derivative of this relation with respect to energy, that is, $T = 1/[\partial S(E, n, \beta)/\partial E]$. On the energy versus entropy graph temperature is represented by the slope of the stable-equilibrium-state curve.

On Figure 5 we see clearly that the slope of the stable-equilibrium-state curve at state A_1 is higher than at state B_1, that *is,* $T_1^A > T_1^B$.

Now we consider the possible effects of an interaction between A and B only that transfers an infinitesimal amount of energy $\delta E^{A\to B}$ from A to B. First we show that, for the given initial states, $\delta E^{A\to B}$ cannot be negative, that is, the energy exchange cannot be from B to A. Indeed, if system B gives out the energy $\delta E^{B\to A}$ it also has to give out an amount of entropy at least equal to $\delta E^{B\to A}/T_1^B$, i.e., $\delta S^{B\to A} \geq \delta E^{B\to A}/T_1^B$ (see Figure 6). But by receiving the energy $\delta E^{B\to A}$ system A can accomodate only an amount of entropy at most equal to $\delta E^{B\to A}/T_1^A$, i.e., $\delta S^{B\to A} \leq \delta E^{B\to A}/T_1^A$. This amount is less than $\delta E^{B\to A}/T_1^B$ for $T_1^B < T_1^A$. So we conclude that the energy (and entropy) exchange can only be from A to B i.e., from the system at high temperature to that at low temperature. This conclusion coincides with the historical statement of the second law given by Clausius.

Next, we show that for a given amount of energy $\delta E^{A\to B}$ transferred from A to B, the accompanying amount of entropy $\delta S^{A\to B}$ is not uniquely and unambiguously determined unless additional restrictions are imposed (see Figure 7). Indeed, if system A gives out the energy $\delta E^{A\to B}$ it also has to give out an amount of entropy at least equal to $\delta E^{A\to B}/T_1^A$, and if system B receives the energy $\delta E^{A\to B}$ it can accomodate an amount of entropy at most equal to $\delta E^{A\to B}/T_1^B$. Thus, for $T_1^A > T_1^B$ we conclude that

$$\frac{\delta E^{A\to B}}{T_1^A} \leq \delta S^{A\to B} \leq \frac{\delta E^{A\to B}}{T_1^B} \tag{1}$$

or, equivalently, that the ratio of energy exchanged and entropy-exchanged is not uniquely determined but can take any value within the range between T_1^B and T_1^A, i.e.,

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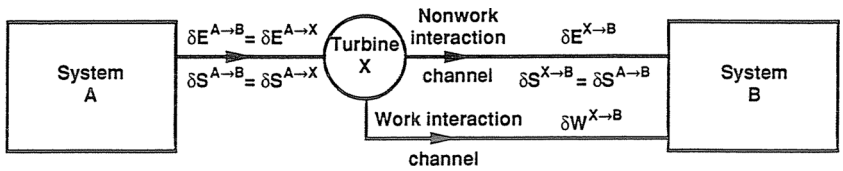


Fig. 10 See text

$$T_1^B \leq \frac{\delta E^{A\to B}}{\delta S^{A\to B}} \leq T_1^A \tag{2}$$

Such indefiniteness is not acceptable because it does not allow us to identify exactly the system in which entropy is generated either in the course of or subsequent to the interaction. For example, Figures 8 and 9 show two extreme cases. In Fig. 8, $\delta S^{A\to B} = \delta E^{A\to B}/T_1^A$, system B receives less entropy than the amount it can accomodate, ends in a state B_2 that is not stable equilibrium, and subsequently evolves spontaneously and irreversibly toward the stable equilibrium B_3. In this case, entropy δS_{irr}^B is generated by irreversibility only within system B. In Figure 9, $\delta S^{A\to B} = \delta E^{A\to B}/T_1^B$, entropy δS_{irr}^A is generated by irreversibility only within system A, and system B ends in stable equilibrium state B_2. In intermediate cases, some entropy is generated by irreversibility in A and some in B. We conclude that the definition of heat as an interaction between two systems at different temperatures is ambiguous, and does not uniquely specify the entropy generated by irreversibility in each of the interacting systems.

To remove this ambiguity, we define a heat interaction as an exchange of energy that is entirely distinguishable (not just different) from work, and that occurs between two systems at different temperatures.

To illustrate clearly what we mean, we consider the systems A and B in Figure 10. The two systems are initially in stable equilibrium states A_1 and B_1 as sketched in Figure 5, and as a result of their interaction the energy exchange is $\delta E^{A\to B}$, and the entropy exchange $\delta S^{A\to B}$. The interaction is clearly different from work because there is an entropy exchange. But to guarantee that the interaction be entirely distinguishable from work we must verify that the same exchanges cannot be possibly achieved by other means that involve a work interaction. For example, the exchanges between A and B could be achieved through a turbine X that takes in the flow of energy and entropy from A, and separates it into a flow of energy and entropy delivered to B through one channel and a flow of energy only (no entropy) delivered to B by means of a work interaction through another channel (the shaft of the turbine).

For the given initial states A_1 and B_1 and the given exchanges $\delta E^{A\to B}$ and $\delta S^{A\to B}$, how much energy could the turbine X deliver to B by means of a work interaction? As shown graphically in Figure 11, the turbine X receives from A the energy $\delta E^{A\to X} = \delta E^{A\to B}$, and at least the entropy $\delta E^{A\to B}/T_1^A$, i.e., $\delta S^{A\to X} \geq \delta E^{A\to B}/T_1^A$. It delivers the same amounts to B through two different channels—two separate interactions. All the entropy from A to X must flow from X to B through the nonwork channel. To accommodate an amount of entropy $\delta S^{X\to B} = \delta S^{A\to X}$ (we assume no entropy generated by irreversibility within X), system B must receive an amount of energy at least equal to $T_1^B \delta S^{A\to X}$ i.e., $\delta E^{X\to B} \geq T_1^B \delta S^{A\to X} \geq T_1^B \delta E^{A\to B}/T_1^A$. The difference $\delta E^{A\to X} - \delta E^{X\to B}$ flows to B through the work interaction channel, that is,

$$\delta W^{X\to B} = \delta E^{A\to X} - \delta E^{X\to B} \leq \left(1 - \frac{T_1^B}{T_1^A}\right)\delta E^{A\to B} \tag{3}$$

where the equal sign holds if both A and B end in stable equilibrium states.

If $T_1^A \neq T_1^B$, we see that the work $\delta W^{X\to B}$ differs from zero and, therefore, that the interaction for B is not entirely distinguishable from work.

An exception to this conclusion obtains when the temperatures T_1^A and T_1^B of the two interacting systems differ at most by an infinitesimal amount, i.e., when $(1 - T_1^B/T_1^A) \ll 1$, because then and only then $\delta W^{X\to B}$ is infinitesimal with respect to the energy exchange $\delta E^{A\to B}$, and the interaction entirely distinguishable from work.

So heat is an exchange of energy and entropy that is determined by an infinitesimal temperature difference, and that is entirely distinguishable from work. Under these conditions, i.e., in the limit as $T_1^A \to T_1^B$, Relation 1 becomes

$$\delta S^{A\to B} = \frac{\delta E^{A\to B}}{T_Q} \tag{4}$$

where T_Q denotes the almost common value of the temperatures T_1^A and T_1^B of the two interacting systems. Thus the ambiguity is removed and the relation between energy exchange and

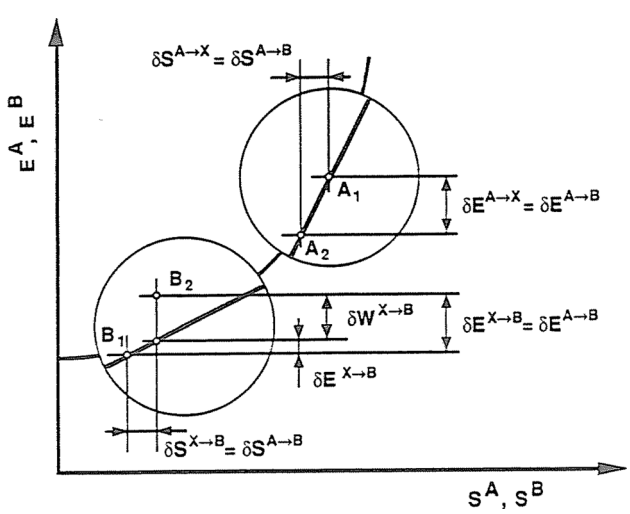
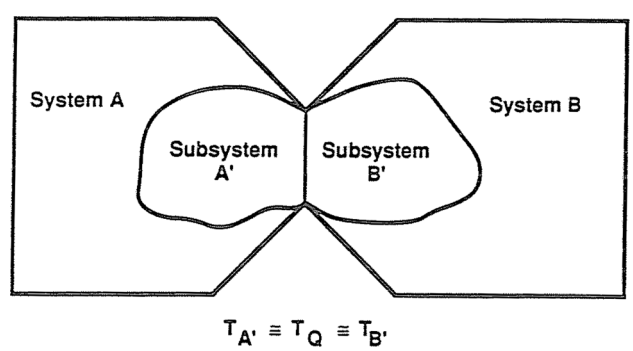


Fig. 11 See text



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entropy exchange is uniquely determined. The amount of energy exchanged in a heat interaction is called heat, and traditionally denoted with the symbol Q instead of E, i.e., the heat is $\delta Q^{A\to B} = \delta E^{A\to B}$.

To be heat an interaction requires that the interacting systems be in stable equilibrium states at about the same temperature. Such systems however may be part of larger systems that are not in stable equilibrium states. For example, we may consider systems A and B that contain subsystems A' and B' respectively, as sketched in Figure 12. Even though systems A and B may not be in stable equilibrium states, the two subsystems A' and B' are in stable equilibrium states, and almost in mutual stable equilibrium at an almost common temperature T_Q. If the interaction between A and B is localized to A' and B', then the conditions for a heat interaction are satisfied, and we can characterize the interaction between the larger systems A and B as heat. In all likelihood, this heat interaction is followed by irreversible spontaneous processes of A and B during which the energy and entropy exchanged in the course of the heat interaction are redistributed between A' and the rest of system A, and B' and the rest of system B.

5 Conclusions

Work and heat are ingenious concepts that allow the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions. These two concepts provide us with practical means for identifying opportunities to reduce the entropy generation by irreversibility and, hence, to improve the performance of a system. These opportunities could be missed if the definition of heat is ambiguous and not sufficiently restrictive.

In this paper, we point out that heat is not a primitive concept and that without the first and second laws of thermodynamics heat and work cannot be distinguished and, therefore, a satisfactory definition of heat cannot be given prior to a statement of these laws. We explain how the laws of thermodynamics can be presented without need for heuristic definitions of heat and temperature, by proceeding gradually from concepts of elementary physics with an approach that we have developed and taught to engineering classes for more than twenty years. We show, with the help of energy versus entropy graphs, that even if introduced after the definitions of energy, entropy, energy and entropy exchange, stable equilibrium state, and temperature, the definition of heat as an exchange of energy that differs from work and is determined by a temperature difference is insufficient to specify a definite and unambiguous relation between the energy and the entropy exchanges. To remove the ambiguity, the definition of a heat interaction must be more restrictive. We define heat as an exchange of energy that is entirely distinguishable (not just different) from work and turns out to be characterized by an infinitesimal temperature difference between the interacting systems.

Appendix: Heat in Terms of Energy and Entropy Not Vice Versa

We outline briefly the logical sequence of our detailed exposition of the foundations of thermodynamics in Ref. 12. We do this not only to show in which way it is possible to present the laws of thermodynamics without resorting to heuristic definitions of heat and temperature, but also to emphasize that this is done by building gradually upon the sophomore background in physics, thus providing continuity in the development of a student's understanding of natural phenomena.

We begin with kinematics and dynamics. In kinematics, we discuss the definitions of system, property, and state. The concept of state that we define provides the common thread for the unification of the various branches of physics without need to modify its meaning from branch to branch. The state is the set of instantaneous values of all the amounts of constituents, ail the parameters that characterize the external forces, and all the properties. Without alteration, this definition is valid for any system, macroscopic or microscopic, and any condition, changing or not changing with time.

In dynamics, we discuss spontaneous and induced changes of state as functions of time, i.e., we introduce the idea of the equation of motion of a system. Certain time evolutions obey Newton's equation of motion or its quantum-mechanical equivalent—the Schrödinger equation of motion. Other experimentally observed time evolutions, however, do not obey either of these equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion that describes all physical phenomena remains a subject of research at the frontier of science—one of the most intriguing and challenging problems in physics. Among the many features that have already been discovered, the most general and well established are captured by the statements of the first law and the second law of thermodynamics. We note that from these two laws derive the most powerful tools to investigate time dependent phenomena.

We introduce a carefully worded and unambiguous statement of the first law in terms of the concept of state and the definition of a weight process. We show that one of the principal implications of this statement is the existence of the property that we call energy and denote by E. Energy is defined for all systems and all states, and is an additive property. It obeys a conservation principle, i.e., it remains invariant in the course of spontaneous changes of state of an isolated system. Because changes of state require a finite time to occur, the principle of energy conservation implied by the first law is an aspect of time evolution. As such, it reflects a special feature of the general equation of motion, even though the equation itself remains to be discovered.

Other implications of the first law are the impossibility of a perpetual motion machine of the first kind, the relation of the law to relativity and mass, and the energy balance. The energy balance is the most universal and powerful tool used in the analysis of practically every physical phenomenon.

Next, we recognize that at a given instant of time a system can be found in one of many different states. We classify each state according to its time evolution, and define unsteady, steady, nonequilibrium, unstable equilibrium, metastable equilibrium, and stable equilibrium states.

We recall that equilibrium is not always stable, and raise the question: "Among all the states of a system that correspond to a given value of the energy, are there any that are stable equilibrium?" Close scrutiny of this question reveals that the answer cannot be found by means of the theory of mechanics. And yet experience shows that such stable equilibrium states exist. The answer is provided by the second law of thermodynamics.

We introduce a carefully worded and unambiguous statement of the second law in terms of the concepts of energy, stable equilibrium state, and reversible process. This statement is an outgrowth of the pioneering work by Hatsopoulos and Keenan. In due course we show that our statement entails all correct statements of the second law that have appeared in the literature. We emphasize that the second law implies the existence of stable equilibrium states but does not require that all states be stable equilibrium. Indeed, the vast majority of states are nonequilibrium. The requirement that some equilibrium states must be stable reflects a most important feature of the general equation of motion, even though this equation remains to be discovered.

The two laws of thermodynamics have many important and practical implications. One of these implications, is the impossibility of a perpetual motion machine of the second kind. Another is that, in general, not all the energy of a system can be transferred to a weight in a gravity field. Under the broad restrictions that

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define a weight process, the amount of energy that can be transferred from a system to a weight depends on the state of the system. If it is not a stable equilibrium state, at least a fraction of the energy can be transferred to the weight. But, if it is a stable equilibrium state, no energy can be transferred to the weight. This limitation reflects innumerable experimental observations, but cannot be accounted for by the principles of mechanics alone. It is one of the important implications of the two laws of thermodynamics.

We prove the existence of a novel important property that we call adiabatic availability and denote by Ψ. The adiabatic availability of a system in a given state is related to the optimum amount of energy that can be exchanged between the system and a weight in a weight process. Like energy, this property is well defined for all systems and all states. Unlike energy it is not additive.

In striving to define an additive property that captures the important features of adiabatic availability, we introduce a special reference system, called a reservoir, and discuss the possible weight processes that the composite of a system and the reservoir may experience. We prove the existence of another important property that we call available energy with respect to a given reservoir, and denote by Ω^R. The available energy of a system in a given state is the adiabatic availability of the composite of the system and the reservoir. It is a generalization of the concept of motive power of fire first introduced by Carnot. Like energy and adiabatic availability, it is a well defined property for all systems and all states, but depends on the reference reservoir.

Finally, we disclose the existence of the property that we call entropy, and denote by S. Entropy is defined in terms of energy, available energy with respect to an arbitrarily selected reservoir, and a constant that depends on the reservoir. In terms of symbols the definition is

$$S = S_o + \frac{1}{c_R}\left[(E - E_o) - (\Omega^R - \Omega^R_o)\right] \tag{A1}$$

where E_o and Ω^R_o refer to an arbitrary reference state, S_o is a constant fixed once and for all for the system, and the constant c_R is a carefully defined property of the reservoir. We prove that the role of the reservoir is only auxiliary, i.e., that the value of S is independent of any characteristics of the arbitrarily selected reservoir. Because both E and Ω^R are defined for all systems (macroscopic as well as microscopic) and all states (equilibrium as well as nonequilibrium), S is also defined for all systems and all states, including a system with one degree of freedom in any of its states.

The concept of entropy introduced here differs from and is more general than that of most textbooks where, as Callen [14] stresses, the existence of the entropy is postulated only for equilibrium states and the postulate makes no reference whatsoever to nonequilibrium states.

We show that entropy obeys a principle of nondecrease, i.e., it either remains invariant or increases in the course of spontaneous changes of state of an isolated system. We show that a spontaneous process is irreversible if the entropy increases, and we call such increase a creation or generation of entropy within the system. Like the principle of energy conservation, the principle of nondecrease of entropy is an aspect of the time evolution and, as such, it reflects another special feature of the general equation of motion that remains to be discovered. We finally introduce the entropy balance which is another powerful tool for analyses of physical phenomena.

At this stage of our exposition, energy and entropy are fully and rigorously defined for equilibrium as well as nonequilibrium states. The concepts of temperature and heat have not yet been either defined or used. As already emphasized, this fact is a most distinguishing feature of our exposition of thermodynamics.

Next we focus our attention on the stable equilibrium states. We show that at a stable equilibrium state the value of any property is fully and uniquely determined by the values of the energy, the amounts of constituents, and the parameters. This conclusion is known as the state principle. It is reached without any extraneous considerations, such as lack of information, difficulty associated with complicated calculations, unpredictability of initial conditions, or lack of interest in making detailed analyses of large systems.

We derive the highest entropy principle and the lowest energy principle as useful criteria for stable equilibrium. We discuss a special form of the state principle known as the fundamental relation. It avers that the value of the entropy at a stable equilibrium state is uniquely determined by the values of the energy, the amounts of constituents, and the parameters. Again, this is a rigorous and general result, involving no approximation whatsoever.

We use the highest entropy principle to investigate necessary conditions that must be satisfied for two systems to be in mutual stable equilibrium, i.e., for the combination of the two systems to be in a stable equilibrium state. These investigations disclose the existence of properties that are defined only for stable equilibrium states, namely, temperature, total potential of a constituent, and pressure. Each of these properties is defined in terms of a partial derivative of the fundamental relation, and is readily measureable. More importantly, we show that necessary conditions for systems to be in mutual stable equilibrium are temperature equality, total potential equality for each constituent, and pressure equality. Each of these equalities provides the theoretical foundation for the measurement of the respective property.

At this stage, we are finally ready to introduce work and heat interactions. A work interaction is defined by the condition that its result be a net exchange of energy between the interacting systems involving no exchange of entropy. We call nonwork any interaction that is not work. A heat interaction is only a special nonwork interaction.

A heat interaction is defined by the condition that it be entirely distinguishable from work—no part of a heat interaction be mistakable as a work interaction. We prove that such an interaction exists, results in a net exchange of both energy and entropy, requires that the interacting systems be almost at the same temperature, and is such that the ratio of the amount of energy exchanged to the amount of entropy exchanged equals the almost common temperature of the interacting systems.

We discuss the energy balance and the entropy balance for a system experiencing only work and heat interactions. The change in energy equals the sum of the work and the heat to the system. This result is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called "the first law". The change in entropy equals the entropy supplied by the heat interaction plus the entropy generated spontaneously by irreversibility within the system. Also this result is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called "the second law".

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

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