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The Concepts of Entropy and Temperature and a New Theory of Macroscopic Thermodynamics

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Abstract

A new macroscopic theory of thermodynamics is presented in which entropy and temperature are introduced using only the effects of adiabatic and diathermal walls on the possible changes of state of a thermodynamic system. Quasistatic heat, defined separately in terms of internal energy and quasistatic work, is then used to establish quantitative measures of entropy and temperature directly by means of new postulates equivalent to the second law of thermodynamics. The third law of thermodynamics is included to complete the theory.

Keywords: Entropy, temperature, macroscopic thermodynamics, laws of thermodynamics.

1. Introduction

1.1 Traditional Thermodynamic Theory

The traditional presentation of macroscopic equilibrium thermodynamics may be summarized as follows (Zemansky, 1951)[1]:

First, the existence of temperature is deduced from the zeroth law. Next, the existence of internal energy is deduced from the first law, and it is concluded that there exists a non-mechanical method of energy transfer, namely heat.

Two statements of the second law are then given: the Kelvin-Planck statement and the Clausius statement. These two statements are proved to be logically equivalent, and are used to prove that no cyclic engine operating between two given reservoirs can be more efficient than a Carnot engine. Then the Kelvin temperature scale is constructed, and it is proved that the integral $\int dQ/T$ around a cycle is zero, where Q is heat and T is the Kelvin temperature. The existence of entropy is deduced from this theorem. The principle of increase of entropy is then established, and is used to associate entropy with molecular disorder.

1.2 Difficulties with Traditional Theory

Traditional thermodynamic theory, which grew out of the history of the subject, was criticized early in the 20th century by Born [2], and the subject was later reopened by Landsberg [3] and other authors (see below) but there is still uneasiness among scientists regarding the logic of macroscopic theory. Here are some of the difficulties:

- There are differing opinions in the literature on the significance of the zeroth law in thermodynamic theory (see the Appendix below).
- The word "work" is used with different meanings, such as work defined for a pressure-volume system by the integral
- $-\int PdV$, and work done when the system is stirred with a paddle wheel.
- The use of "impossibility" statements in the Kelvin-Planck and Clausius forms of the second law is awkward.
- The Kelvin-Planck and Clausius statements suggest that the second law of thermodynamics depends on the properties of heat engines and refrigerators, even

though it is applied in fields unrelated to engineering.

- The existence of entropy seems to depend on heat, Carnot cycles, and the Kelvin temperature scale.
- The fact that entropy is related to molecular disorder cannot be made clear in purely macroscopic terms.

1.3 Alternative Theories

There have been many attempts to improve the theory of macroscopic thermodynamics, beginning with the work of Caratheodory (1909) [4]. Unfortunately Caratheodory's theory is difficult for all except mathematical specialists. Other detailed mathematical studies include those of Falk and Jung (1959)[5], Boyling (1972)[6], Callen (1985)[7], and the recent work of Lieb and Yngvason (1998)[8, 9].

Yet the underlying statistical basis of thermodynamics is simple in principle, so we should be able to construct a correspondingly simple macroscopic theory.

1.4 A New Theory

This paper gives a new macroscopic theory of equilibrium thermodynamics designed to overcome the difficulties mentioned above (Exell, 1985, 1996)[10, 11]. The concepts and postulates used are inspired by the underlying statistical basis of thermodynamics, and are arranged in a simple logical structure. They characterize the properties of thermodynamic systems directly, and could in principle be demonstrated experimentally.

Every logical theory begins with undefined terms representing the entities under discussion; these terms must be introduced by description and example. In the text below the undefined terms, and the important defined terms, are printed in bold type. The axioms of equivalence and simple ordering are used to characterize certain relations with which the theory is concerned. These axioms are not regarded as laws or postulates of thermodynamics.

The properties of a thermodynamic system that we can observe macroscopically depend on the properties of the walls of the system's container. Entropy and temperature are thermal properties of a system indicating the behavior of the system when it is separated from its environment by thermally insulating walls, or is in thermal contact with its environment through thermally conducting walls. The first and second laws of thermodynamics, as postulated in this theory, then give quantitative measures of entropy and temperature in terms of heat.

The zeroth law of thermodynamics is not needed as a basic postulate. The reasons for this are explained in an Appendix.

2. Properties of Thermodynamic Systems

2.1 Closed Thermodynamic Systems

The theory is restricted to closed thermodynamic systems. A **closed thermodynamic system** is a quantity of matter separated from its **environment** by a container. The system has a set of **equilibrium states**. These equilibrium states are the basic elements of the theory.

A **transition** is a change from one equilibrium state to another. The theory is about what transitions are possible and what energy exchanges occur between the system and its environment during transitions. During a transition a system may pass through non-equilibrium states. In such cases the theory deals only with the relation between the end states and with the total effect of the transition; it cannot deal with the non-equilibrium states between the end states.

2.2 Mechanical Properties and Isometric Sets

The equilibrium states of a thermodynamic system are characterized by pairs of **non-thermal macroscopic variables** such as pressure and volume, magnetic field and magnetic dipole moment, etc. The product of each pair of non-thermal variables has the dimensions of energy. For simplicity in this presentation of the theory we consider systems in which the only non-thermal variables are **pressure** P and **volume** V, and the pair (P,V) denotes an equilibrium state of the system.

Unfortunately, pressure and volume alone do not always define the equilibrium state uniquely. For example, at a pressure of one atmosphere, one kilogram of liquid water has volume 1.00016 liters at 0°C, 1.00002 liters at 4°C, and 1.00016 liters again at 8°C. We shall suppose, however, that different equilibrium states with the same pressure and volume can be distinguished by observations in some other way.

A non-thermal variable which can be freely controlled, and whose change involves the performance of work on the system, is called an **external parameter**. A set of equilibrium states in which all the external parameters are constant is called an **isometric set**. In a pressure-volume system the external parameter is volume, and all the states in an isometric set have the same volume. When the walls of the system's container are rigid we can measure the system's volume V, which is independent of the properties of the environment.

The environment of a thermodynamic system may have a high pressure or a low pressure. When the walls are flexible or movable, so that the volume of the system can change in response to changes in the pressure of the environment, the system is in *mechanical contact* with the environment. A state that remains unchanged when the system is in mechanical contact with the environment is said to be in **mechanical equilibrium** with the environment, and the pressure of the system is the same as the pressure of the environment. A set of states all in mechanical equilibrium with the same environment is called an **isobaric set** because all the states in the set have the same pressure.

Volume and pressure are the basic *mechanical properties* of thermodynamic systems related to the *movability* of the walls of the container.

2.3 Adiabatic Walls and Isentropic Sets

In this section the concept of entropy is introduced qualitatively by Buchdahl's method [12].

The environment of a thermodynamic system may be hot or cold. If the system is in a container with thermally insulating walls, then changes in the environment from hot to cold, or cold to hot, do not cause any change in the equilibrium state of the system. The thermally insulating walls are called **adiabatic walls**. Any change of state of a system separated from its environment by adiabatic walls is called an **adiabatic transition**.

Imagine a thermodynamic system that consists of a fluid (e.g. liquid and vapor) in a container with adiabatic walls. Experience shows that when the state of the system is changed by slowly changing the volume it is possible to reverse the process and return the system to its initial state. In other words there exists an adiabatic transition from the initial state to the final state, and an adiabatic transition from the final state to the initial state. We then say that there exists a relation of **mutual adiabatic accessibility** between the two states.

The relation of mutual adiabatic accessibility between states satisfies the axioms of an equivalence relation. Let (P_1,V_1), (P_2,V_2), and (P_3,V_3) denote states, and let $(P_1,V_1) \leftrightarrow (P_2,V_2)$ mean that (P_1,V_1) and (P_2,V_2) are mutually adiabatically accessible from each other. Then, for all (P_1,V_1), (P_2,V_2), and (P_3,V_3):

(1) $(P_1,V_1) \leftrightarrow (P_1,V_1)$.
(2) If $(P_1,V_1) \leftrightarrow (P_2,V_2)$, then $(P_2,V_2) \leftrightarrow (P_1,V_1)$.
(3) If $(P_1,V_1) \leftrightarrow (P_2,V_2)$ and $(P_2,V_2) \leftrightarrow (P_3,V_3)$, then $(P_1,V_1) \leftrightarrow (P_3,V_3)$.

This equivalence relation divides the equilibrium states into equivalence classes called **isentropic sets** Σ. Two states in the same isentropic set are mutually adiabatically accessible from each other.

Now suppose that the state of the same adiabatically enclosed system can be changed in other ways, such as by passing an electric current through a resistor in the fluid, or by stirring the fluid. Experience shows that in these cases the adiabatic transitions are irreversible; there exists an adiabatic transition from the initial state to the final state, but not from the final state to the initial state. We say that a relation of **one-way adiabatic accessibility** exists from the initial state to the final state. If the initial state is (P_1,V_1) and the final state is (P_2,V_2), we write $(P_1,V_1) \rightarrow (P_2,V_2)$.

Let (P_1,V_1) be any state in an isentropic set Σ_1, and let (P_2,V_2) be any state in a *different* isentropic set Σ_2. *Experience shows that either* $(P_1,V_1) \rightarrow (P_2,V_2)$ *or* $(P_2,V_2) \rightarrow (P_1,V_1)$. If $(P_1,V_1) \rightarrow (P_2,V_2)$, then every state in Σ_2 is one-way adiabatically accessible from every state in Σ_1 via (P_1,V_1) and (P_2,V_2). In other words, the one-way adiabatic accessibility relation holds from Σ_1 to Σ_2, and we write $\Sigma_1 \rightarrow \Sigma_2$.

The one-way adiabatic accessibility relation between isentropic sets satisfies the axioms for a simple order relation. For all Σ_1, Σ_2, and Σ_3:

(1) Exactly one of the following relations is true: $\Sigma_1 \to \Sigma_2$, $\Sigma_1 = \Sigma_2$, $\Sigma_2 \to \Sigma_1$.
(2) If $\Sigma_1 \to \Sigma_2$ and $\Sigma_2 \to \Sigma_3$, then $\Sigma_1 \to \Sigma_3$.

Axiom (1) is true because, as explained above, it is true for the individual states in Σ_1 and Σ_2. To see that axiom (2) is true note that if the conclusion is false, then there exists an adiabatic transition from every state in Σ_3 to every state in Σ_1. This implies that if $\Sigma_1 \to \Sigma_2$ is true then $\Sigma_2 \to \Sigma_3$ is false, and if $\Sigma_2 \to \Sigma_3$ is true then $\Sigma_1 \to \Sigma_2$ is false. In other words, the hypothesis is false.

The ordered system of isentropic sets can now be labeled with *numerical entropies* consistent with the ordering. The entropy is defined quantitatively in Section 4.1 below.

2.4 Diathermal Walls and Isothermal Sets

In this section the concept of temperature is introduced qualitatively by a new method similar to Buchdahl's method of introducing entropy.

A thermodynamic system may be in thermal contact with its environment through a thermally conducting wall. A thermally conducting wall is called a **diathermal wall.** A state that remains unchanged when the system is in thermal contact with its environment is said to be in **thermal equilibrium** with its environment. If the volume of a system in thermal contact with its environment is changed, the pressure changes spontaneously to keep the system in thermal equilibrium with the environment.

Two states in thermal equilibrium with the same environment are said to be in **mutual thermal equilibrium** with each other. The relation of mutual thermal equilibrium satisfies the axioms of an equivalence relation. Let $(P_1,V_1) \sim (P_2,V_2)$ mean that (P_1,V_1) and (P_2,V_2) are in mutual thermal equilibrium with each other. Then, for all (P_1,V_1), (P_2,V_2), and (P_3,V_3):

(1) $(P_1,V_1) \sim (P_1,V_1)$.
(2) If $(P_1,V_1) \sim (P_2,V_2)$, then $(P_2,V_2) \sim (P_1,V_1)$.
(3) If $(P_1,V_1) \sim (P_2,V_2)$ and $(P_2,V_2) \sim (P_3,V_3)$, then $(P_1,V_1) \sim (P_3,V_3)$.

This equivalence relation divides the set of equilibrium states into equivalence classes called **isothermal sets** Θ. Two states in the same isothermal set are in mutual thermal equilibrium with each other.

Now suppose that the volume of the system is fixed and the thermal property of the environment is changed (from hot to cold or from cold to hot). A spontaneous transition occurs from the initial state to a final state in thermal equilibrium with the second environment. When the final state is one-way adiabatically accessible from the initial state, the final state is said to be **hotter than** the initial state, and the second environment is hotter than the first environment; then, if the initial state is (P_1,V_0) and the final state is (P_2,V_0), we write $(P_1,V_0) << (P_2,V_0)$.

Let (P_1,V_1) be any state in an isothermal set Θ_1, and let (P_2,V_2) be any state in a *different* isothermal set Θ_2. Let (P_{12},V_2) be in Θ_1 and let (P_{21},V_1) be in Θ_2. *Experience shows that either* $(P_1,V_1) << (P_{21},V_1)$ *and* $(P_{12},V_2) << (P_2,V_2)$, *or* $(P_{21},V_1) << (P_1,V_1)$ *and* $(P_2,V_2) << (P_{12},V_2)$. In other words, a unique hotter-than relation holds between Θ_1 and Θ_2 which is independent of the choice of the fixed volume.

The hotter-than relation between isothermal sets satisfies the axioms for a simple order relation. For all Θ_1, Θ_2, and Θ_3:

(1) Exactly one of the following relations is true: $\Theta_1 << \Theta_2$, $\Theta_1 = \Theta_2$, $\Theta_2 << \Theta_1$.
(2) If $\Theta_1 << \Theta_2$ and $\Theta_2 << \Theta_3$, then $\Theta_1 << \Theta_3$.

These axioms are true for the isothermal sets because they are true for the adiabatic accessibility relation between individual states with a fixed volume.

The ordered system of isothermal sets can now be labeled with *numerical temperatures* consistent with the ordering. The temperature is defined quantitatively in Section 4.1 below.

3. The First Law of Thermodynamics

3.1 The First Law and Internal Energy

The Principle of Conservation of Energy and the First Law of Thermodynamics are separate ideas in this theory. The **Principle of Conservation of Energy** states that *energy cannot be created or destroyed.* If energy seems to appear or disappear, then we can always find a new form of energy which accounts for the discrepancy. Our statement of the **First Law of Thermodynamics** is based on that of Caratheodory:

The amount of energy transferred to or from a thermodynamic system in an adiabatic transition – measured by work done in the system's environment – depends only on the initial and final equilibrium states.

This statement characterizes adiabatic transitions as those in which the energy change in the environment is measurable entirely as mechanical work.

Suppose that any three equilibrium states are given. We may number the states 1, 2, and 3 so that the following adiabatic transitions exist: (P_1,V_1) to (P_2,V_2), (P_2,V_2) to (P_3,V_3), and (P_1,V_1) to (P_3,V_3). Let E_{12} be the energy transferred to the system in an adiabatic transition (P_1,V_1) to (P_2,V_2), and let E_{23} be the energy transferred to the system in an adiabatic transition (P_2,V_2) to (P_3,V_3). Then, by the first law, the energy E_{13} transferred to the system in an adiabatic transition (P_1,V_1) to (P_3,V_3) is given by

$$E_{13} = E_{12} + E_{23},$$

whether or not the system passes through the state (P_2, V_2).

It follows from this fact, and from the principle of conservation of energy, that we may define an **internal energy** potential U for the equilibrium states such that $U(P_3,V_3) - U(P_1,V_1) = E_{13}$.

3.2 Quasistatic Paths, Quasistatic Work, and Quasistatic Heat

A path in the set of equilibrium states through a succession of neighboring states is called a **quasistatic path**. For each quasistatic path we define the **quasistatic work** W by

$$W = -\int P dV,$$

where the integral is from an initial state (P_1,V_1) to a final state (P_2,V_2) along the path. The value of W depends on the path as well as on the initial and final states.

Also, for each quasistatic path we define the **quasistatic heat** Q by

$$U(P_2,V_2) - U(P_1,V_1) = W + Q.$$

Since the value of W depends on the path, but the value of $U(P_2,V_2) - U(P_1,V_1)$ does not, it follows that the value of Q depends on the path.

Quasistatic work and quasistatic heat are properties of quasistatic paths. They must not be confused with mechanical work and heat transfer in real physical processes. However, mechanical work and heat transfer may be practically equal to W and Q in a real process that is practically quasistatic.

4. The Second Law of Thermodynamics

It is now recognized that the second law of thermodynamics can be divided into parts (Kestin, 1976)[13]. In this new theory the first part gives universal measures of entropy and temperature in terms of quasistatic heat. The second part associates the one-way adiabatic accessibility relation with the proper direction of the entropy scale, and the "hotter-than" relation with the proper direction of the temperature scale. The third part is the principle of increase of entropy for spontaneous transitions in unbalanced coupled systems; this is deduced from the first two parts.

4.1 The First Part of the Second Law

The **First Part of the Second Law** consists of the following two postulates.

(1) *On a quasistatic path in an isentropic set* $Q = 0$.

(2) *Let two different environments be given. Choose any thermodynamic system and any pair of isentropic sets in the system. Then the quasistatic heats* Q_1 *and* Q_2 *on isothermal quasistatic paths in thermal equilibrium with the two environments from the first isentropic set to the second are always in the same positive ratio* Q_1/Q_2.

Since Q_1/Q_2 depends only on the environments, and not on the thermodynamic system chosen, nor on the isentropic sets chosen, we define **absolute temperatures** T_1 and T_2 for the two environments by means of the equation

$$T_1/T_2 = Q_1/Q_2,$$

with a standard value $T = 273.16$ kelvins at the triple point of water. The kelvin defined in this way is the universal thermal unit of thermodynamics.

Since the standard value of T at the triple point of water is positive, it follows from postulate (2) that: *All absolute temperatures are positive.*

We can now define an **entropy** potential S for each isentropic set such that for the two isentropic sets chosen

$$S_2 - S_1 = Q_1/T_1 = Q_2/T_2.$$

The first part of the second law and the definitions of absolute temperature and entropy imply that:

Along a quasistatic path we have $dQ = TdS$.

An outline of the proof is as follows: Consider two points close together on the path. Suppose (without loss of generality) that T is non-decreasing and S is monotonic along the given path from point 1 to point 2. Choose a three-step path from point 1 to point 2 as follows:

(a) An isentropic step with entropy S_1 from temperature T_1 to temperature T such that $T_1 \leq T \leq T_2$,
(b) an isothermal step at temperature T from entropy S_1 to entropy S_2,
(c) an isentropic step with entropy S_2 from temperature T to temperature T_2.

The temperature T is chosen so that *the quasistatic work along the three-step path is the same as the quasistatic work W along the given path.* By the first law of thermodynamics, we have along the given path $U_2 - U_1 = W + Q$, where Q is the quasistatic heat. Therefore, since $U_2 - U_1$ is the same for any path, the quasistatic heat along the three-step path is also Q. By postulate (1) in the first part of the second law, the quasistatic heat is zero in steps (a) and (c). By the definition of entropy, the quasistatic heat is $T(S_2 - S_1)$ in step (b). Therefore $Q = T(S_2 - S_1)$. By making point 1 and point 2 closer and closer together we obtain in the limit

$$dQ = TdS.$$

Note that in a transition from a given initial state to a given final state the entropy difference $S_2 - S_1$ between the states is the same for all possible processes. In particular, *along any quasistatic path* from the initial state to the final state

$$S_2 - S_1 = \int dQ/T.$$

4.2 Second Part of the Second Law

The **Second Part of the Second Law** consists of the following two postulates.

(3) *A state with entropy S_2 is one-way adiabatically accessible from a state with entropy S_1 if and only if $S_1 < S_2$.*
(4) *A state with absolute temperature T_2 is hotter than a state with absolute temperature T_1 if and only if $T_1 < T_2$.*

A corollary of postulate (3) is that: *When a system gains heat the initial state is adiabatically inaccessible from the final state.*

To prove this, note that along any quasistatic path from the initial state to the final state $S_2 - S_1 = \int dQ/T$. Since T is always positive, a positive quasistatic heat implies that $S_1 < S_2$. Therefore, by postulate (3) above, the final state is one-way adiabatically accessible from the initial state. In other words, the initial state is adiabatically inaccessible from the final state.

A corollary of postulate (4) is that: *A system at a higher absolute temperature than its environment loses heat to the environment when placed in thermal contact with it.*

To prove this, note that, by postulate (4), the system is initially hotter than the environment. Therefore, by the definition of "hotter than", the initial state is one-way adiabatically accessible from a final state in thermal equilibrium with the environment. It follows from the corollary of postulate (3) just proved (with the initial and final states interchanged) that the system loses heat when placed in thermal contact with the environment.

4.3 An Application to Mechanics: The Carnot Cycle

It can be shown from the first and second parts of the second law that the most efficient cycle for a heat engine converting heat into work is the Carnot cycle.

The proof is based on the fact that the system, after increasing its entropy by absorbing heat at a high absolute temperature, must reject some heat at a low absolute temperature to return to its initial entropy. The greatest amount of mechanical work is obtained when the heat rejected is the least. This means that (a) the heat should be absorbed without any temperature difference between the source and the working thermodynamic system, (b) the rejection of heat should be at the lowest possible temperature, and (c) the entropy produced by irreversibilities should be zero.

The Kelvin-Planck and Clausius statements of the second law of thermodynamics are corollaries of this result.

4.4 The Third Part of the Second Law: The Principle of Increase of Entropy

Imagine two closed thermodynamic systems surrounded by adiabatic walls and coupled by a movable adiabatic wall so that changes in volume of the two systems satisfy the equation $\Delta V_1 + \Delta V_2 = 0$. Each system may be regarded as the environment of the other system. Suppose that initially the pressures are unequal with $P_1 < P_2$, and after the movable wall is released it comes to rest with the final pressures equal. It follows from the laws of mechanics that $\Delta V_1 < 0$, and $\Delta V_2 > 0$.

We can imagine quasistatic paths from the initial states to the final states. In these quasistatic paths the total quasistatic work $W_1 + W_2$ is negative because $P_1 < P_2$, $\Delta V_1 < 0$, and $\Delta V_2 > 0$. But the total change in internal energy $\Delta U_1 + \Delta U_2$ is zero. Therefore the total quasistatic heat is positive. Since the walls are adiabatic, it follows from the equation $dQ = TdS$ that the sum of the entropies of the two systems increases.

In this example the quasistatic heat is produced by friction, not by heat transfer, because both systems are surrounded by adiabatic walls.

Imagine two systems with fixed volumes in thermal contact with each other through a diathermal wall, but thermally isolated from the general environment by adiabatic walls. Each system may be regarded as the local environment of the other system. Suppose that initially the temperatures are unequal with $T_1 < T_2$. It follows from the second part of the second law that system 1 gains heat and system 2 loses heat until the two systems reach thermal equilibrium at the same temperature. Therefore, by the first part of the second law, $\Delta S_1 > 0$, and $\Delta S_2 < 0$.

We can imagine quasistatic paths from the initial states to the final states. On these quasistatic paths the quasistatic work is zero, because the volumes are fixed, and the total change in internal energy $\Delta U_1 + \Delta U_2$ is zero; therefore the quasistatic heat gained by system 1 equals the quasistatic heat lost by system 2. But along the path between the initial and final states we have $T_1 < T_2$; therefore, by the equation $dQ = TdS$, we have $|\Delta S_1| > |\Delta S_2|$. Since $\Delta S_1 > 0$ and $\Delta S_2 < 0$, it follows that the sum of the entropies of the two systems increases.

The same result can be proved for two systems thermally isolated from the environment and coupled by a movable *diathermal* wall.

These "thought experiments" prove the following statement, which we call the **Third Part of the Second Law**:

When two coupled systems separated from the environment by adiabatic walls pass spontaneously from an unbalanced condition to mutual equilibrium, the sum of the entropies of the two systems increases.

The general **Principle of Increase of Entropy** is based on this law. Spontaneous natural processes involve changes towards mutual equilibrium in unbalanced coupled systems. By the third part of the second law these changes cause the total entropy of the combined systems to increase.

5. The Third Law of Thermodynamics

The theory may be completed by the following statement of the **Third Law of Thermodynamics**:

On a quasistatic path such that the absolute temperature approaches zero while the external parameters remain bounded, the entropy potential approaches a finite limit S_0 *which is the same for all such paths.*

The **Nernst Heat Theorem** is a corollary of this law. It may be stated as follows:

In a set of equilibrium states with bounded values of the external parameters the entropy difference between two states at the same temperature approaches zero as the absolute temperature approaches zero.

We now define the **absolute entropy** of a system to be the entropy potential obtained by putting $S_0 = 0$. The postulates constituting the second part of the second law imply that, for any pair of states 1 and 2 in an isometric set, $T_2 > T_1$ if and only if $S_2 > S_1$. It follows from the definition of absolute entropy that: *All absolute entropies are positive.*

The third law of thermodynamics has applications in low temperature physics and chemistry, but it is not needed in engineering.

6. Concluding Remarks

It is hoped that the reader will find this theory more direct than other theories, especially as regards the treatment of entropy and temperature. All the relations connecting the internal energy, entropy, and temperature of thermodynamic systems with other macroscopic quantities (such as isothermal compressibility, thermal expansivity, heat capacity, etc.) can be derived on the basis of this theory. But the actual values of thermodynamic quantities are not given by thermodynamic theory; they must be measured in the laboratory, or calculated by statistical mechanics.

Appendix: The Zeroth Law of Thermodynamics

The zeroth law may be stated as follows:

Two thermodynamic systems in thermal equilibrium with the same environment are in thermal equilibrium with each other.

There are two reasons why the zeroth law does not appear as a postulate in this new theory:

1. Redlich has pointed out [14] that there exist experimental situations where the zeroth law fails. For example, a system which emits neutrons, and another system which absorbs neutrons may separately be in thermal equilibrium with the environment; but they will not be in thermal equilibrium with each other because of the neutron interactions. Therefore the zeroth law can be viewed as a characterization of thermal interactions.

2. Turner has shown [15] that the zeroth law is a consequence of the first and second laws of thermodynamics. An argument equivalent to Turner's is as follows: Let systems A and B be in thermal equilibrium with the environment, and suppose that B is hotter than A, *violating the zeroth law*. Expand B reversibly until it is in thermal equilibrium with A. Then put A and B in thermal contact, and compress B reversibly to its original volume. Since B loses heat to A during the compression, the work of compression of B is less than the work of expansion, and there is a net output of work. Finally, let A and B be returned separately by thermal contact to equilibrium with the environment. The overall result is a complete conversion of heat from the environment into work in a cyclic process *violating Kelvin's statement of the second law.*

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