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A Personal View of Macroscopic Equilibrium Thermodynamics

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Abstract: It is argued that the usual way of teaching thermodynamics to students today perpetuates the difficulties that engineers and scientists in the nineteenth century had in understanding how heat engines work. A new theory is outlined that aims to be clearer than the traditional approach.

1. Introduction

The title of this paper may seem to be a contradiction in that the term *Equilibrium* suggests that the systems studied are at rest and the term *Thermodynamics* suggests that they are in motion produced by heat. The reason for this is that the subject was developed by engineers and scientists in the nineteenth century studying engines that produced mechanical power from heat with theories using the properties of the working substances in the heat engines in equilibrium. The term *Macroscopic* indicates that the theories referred only to the bulk properties of the working substances without considering the behavior of the atoms and molecules of which they are composed.

The thermodynamics taught in high schools and universities today is still influenced by the roundabout way in which the subject was developed in the nineteenth century. The students are taught the zeroth, first, and second laws in their old formulations. In advanced courses a third law may be added when it is needed in special areas of chemistry and low temperature physics.

It is a strange fact in the history of thermodynamics that the zeroth, first, and second laws were formulated in the reverse order of their numbering. There were contributions by many authors, but the principal landmarks were as follows. The second law was first stated by Carnot in 1824, the first law was stated by Joule in 1840, and it was not until 1935 that Fowler felt the need to formalize the concept of thermal equilibrium in the zeroth law.

2. Comments on the Traditional Laws of Thermodynamics.

It is my view that the traditional presentation of thermodynamics perpetuates the problems that the early researchers had in formulating the concepts of the subject in the past, and this makes it difficult for students to understand the subject today. A few of my opinions on these matters are given below.

2.1 Comments on the Zeroth Law

The zeroth law is more pedantic than necessary. The law states that if two systems are both in thermal equilibrium with a third system, then the two systems will be in thermal equilibrium with each other. Based on this fact we can devise a temperature scale for indicating the thermal equilibrium of systems. But this kind of equivalence relation holds for any measurement. For example, if on a laboratory balance two weights are both in balance with a third weight, then the two weights will be in balance with each other. Surely it is enough to acknowledge the concept of balancing weights without elevating it to the status of a physical law. Likewise it seems enough to acknowledge the concept of thermal equilibrium without calling it another law of thermodynamics.

Moreover, the temperature scales devised on this basis can only be empirical. They are not the same as the thermodynamic (Kelvin) scale. Even the so called "absolute temperature" of an ideal gas is not conceptually the same as the thermodynamic temperature implied by the second law of thermodynamics.

It can also be argued that the zeroth law is a consequence of the second law. If in Fig. 1 systems 1 and 2 are both in thermal equilibrium with system 3, but systems 1 and 2 are not in thermal equilibrium with each other, violating the zeroth law, then it is possible to use a heat engine to produce work from the combination 123 without rejecting heat to the environment, violating the second law. It follows that the second law implies the zeroth law.

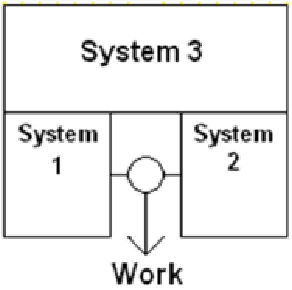

Figure 1. How a violation of the zeroth law would violate the second law.

2.2 Comments on the First Law

It is sometimes said that the first law is the law of conservation of energy in thermal systems. This is only a half truth. The conservation of energy is a more general law independent of thermodynamics. It arises from the fact that the laws of physics are independent of time (Noether's theorem).

The early researchers did not understand correctly the nature of heat. They believed that hot bodies contained a fluid called *caloric* which tended to spread out into other bodies making them hot also, and causing them to expand. This theory was replaced only when the mechanical equivalent of heat had been determined and it was seen that thermodynamic systems have internal energy.

2.3 Comments on the Second Law

The second law was formulated in two ways: by Kelvin, saying that it is impossible for any cyclic device to convert heat completely into work, and by Clausius, saying that it is impossible for any cyclic device to transfer heat from a cold body to a hot body without the expenditure of work. These two formulations were shown to be equivalent, and the reversible Carnot cycle was found to be the most efficient way of operating these machines. The concepts of thermodynamic temperature and entropy were then derived by mathematical arguments from the Carnot cycle.

Understanding the physical meaning of entropy derived in this way from engineering concepts is difficult. Entropy is said to be increased in irreversible processes. Why? This is not implied in the derivation of the entropy concept from the Carnot cycle. Something more is needed. Explanations that fall back on statistical arguments, saying that entropy is a measure of disorder, are improper ways of patching up holes in the macroscopic theory.

2.4 Methods of Reasoning

Some of the concepts and methods of reasoning used by the fathers of thermodynamics can be questioned, such as transfers of heat without a temperature difference, or changes in the state of the working substances while remaining infinitesimally close to equilibrium. A new conceptual framework designed to avoid such questions is described below. A complete account of this theory is given in my 2014 paper listed in the bibliography.

3. Outline of a New Macroscopic Theory

Every logical theory begins with undefined terms introduced by descriptions and examples. Other terms may then be defined from them. These terms represent the entities of the theory and the relations between them. In a physical theory postulates based on induction from experience show what general facts are accepted about these entities and relations. In the basic theory described here important terms are printed in bold type and the postulates are printed in italics.

3.1 Thermodynamic Systems

The theory is restricted to a **simple closed system**, which is a quantity of matter separated from its **environment** by the walls of a container. The system has a set of stable **equilibrium states** Z. Each state has a pair of non-thermal variables: pressure P and volume V.

To illustrate the theory we take dry air modeled as an ideal gas. This model is satisfactory for air under the ordinary conditions found in meteorology and air conditioning.

The environment may be **hot**, such as a bath of boiling water, or **cold**, such as a bath of melting ice. If the walls of the container are **thermally conducting**, then a change in the environment from hot to cold or from cold to hot will cause the equilibrium state of the system to change. If, however, the walls are **thermally insulating**, like the double walls of a vacuum flask, then a change in the environment from hot to cold or from cold to hot will not cause any change in the equilibrium state of the system.

When the state of the system is caused to change and the walls of the container are thermally insulating, the change of state is called **adiabatic**. Experience shows that the following postulate is true.

Postulate 1. *For any pair of stable equilibrium states* Z_1 *and* Z_2 *of a simple closed thermodynamic system an adiabatic change of state is possible from* Z_1 *to* Z_2 *or from* Z_2 *to* Z_1*.*

3.2 Energy and the First Law

Energy can be transferred between the system and its environment by methods such as those shown in Fig. 2. If the walls of the container are thermally insulating the change of state is adiabatic, and the amount of energy transferred to or from the system can measured entirely by mechanical work done in the environment.

We note in passing for future reference that work done by a movement of the wall is **reversible** because the volume may be reduced or increased, so energy can be transferred to or from the system. If, however, an electrical current is passed through the resistor or the weight falls, energy is transferred to the system, but these processes are **irreversible**. It is impossible for energy in the system to make an electrical current flow in the resistor or to lift the weight.

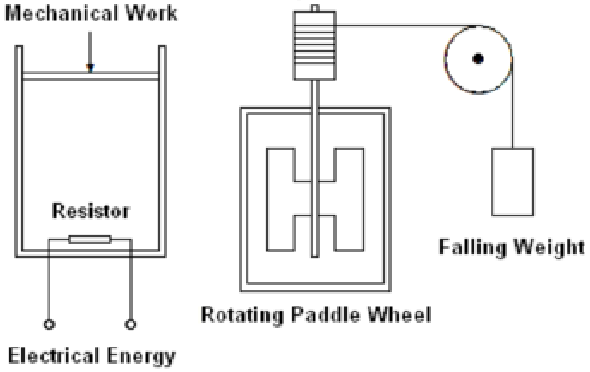

Figure 2. Adiabatic energy transfers between a system and its environment.

The **First Law of Thermodynamics** can now be stated as follows:

Postulate 2. *The amount of energy transferred to or from a thermodynamic system in an adiabatic change of state, measured by work in the environment, depends only on the initial and final states.*

It follows from Postulates 1 and 2, and the Principle of Conservation of Energy, that we may define an **internal energy** potential E on the set of equilibrium states with a reference state Z_0 chosen to have the zero energy potential. The internal energy function must be found by experimental measurements.

Example

The internal energy of air is given by

$$E = 2.5PV.$$

This formula is acceptable under normal conditions, but it cannot be used at low temperatures where the ideal gas laws fail.

The pressure and volume of a simple closed thermodynamic system do not always specify the state of the system uniquely. For example, water at a pressure of one atmosphere has a minimum volume per unit mass just above the melting point of ice. In the neighborhood of this minimum there are different states with the same pressure and volume but different internal energies. Ambiguities such as this are resolved by **The State Principle**, which we present as a third postulate:

Postulate 3. *The stable equilibrium state of a simple closed thermodynamic system is specified uniquely by its volume and its internal energy.*

It follows from this postulate that there is a one-one correspondence between the equilibrium states of a simple thermodynamic system and the points on a two-dimensional E-V diagram.

We now assume that paths, which we call **quasistatic paths**, can be drawn through successions of neighboring equilibrium states, and that differentials defined on the equilibrium states can be integrated along these paths.

We define the differential of **quasistatic work** along a quasistatic path as the energy change produced by a change in volume thus

$$dW = -PdV.$$

But the internal energy can be changed by other means, such as an electrical current in the resistor shown in Fig. 2. To account for this we define the differential of **quasistatic heat** as the difference

$$dQ = dE - dW.$$

Example
For air the differential of the quasistatic heat is

$$dQ = 3.5PdV + 2.5VdP.$$

It follows that

$$dE = 2.5d(PV).$$

This completes our treatment of the first law of thermodynamics. The concept of a measurable temperature has not been used because this belongs to the second law of thermodynamics.

3.3 The First Part of the Second Law: Entropy and Temperature

The second law of thermodynamics may be divided into two parts. The first part is concerned with the definitions and properties of entropy and temperature.

If an adiabatic change of state from Z_1 to Z_2 is **reversible** we write $Z_1 \leftrightarrow Z_2$. This is an equivalence relation that divides the states of the system into equivalence classes which we call **isentropic sets** Σ.

If the adiabatic change of state is **irreversible** we write $Z_1 \rightarrow Z_2$ and for the two isentropic sets that contain these states we write $\Sigma_1 \rightarrow \Sigma_2$. This defines a total ordering of the isentropic sets.

Example
The isentropic sets of air satisfy the equation $PV^{1.4} = constant$, where the constant is different in different isentropic sets. An adiabatic change of state is possible only if the constant in the new state is equal to or greater than the constant in the old state.

If two states Z_1 and Z_2 are both in thermal equilibrium with the same environment through a thermally conducting wall we write $Z_1 \equiv Z_2$. This is another equivalence relation that divides the states of the system into equivalence classes which we call **isothermal sets** Θ.

When two states Z_1 and Z_2 have the same volume and $Z_1 \rightarrow Z_2$ we say Z_2 is **hotter than** Z_1 and for the two isothermal sets that contain these states we write $\Theta_1 \rightarrow \Theta_2$. This defines a total ordering of the isothermal sets.

Example
The isothermal sets of air satisfy the equation $PV = constant$, where the constant is different in different isothermal sets. An isothermal set with a higher value of the constant is hotter than an isothermal set with a lower value of the constant.

The following two postulates allow us to define thermodynamic temperature and entropy.

Postulate 4. *On a quasistatic path in an isentropic set the quasistatic heat is zero.*

Postulate 5. *Let two environments be given. Choose any thermodynamic system and any pair of isentropic sets Σ_1 and Σ_2 in the system. Let Θ_1 and Θ_2 be the isothermal sets in thermal equilibrium with the two environments. Then the quasistatic heats Q_1 and Q_2 on quasistatic paths in the two isothermal sets from one isentropic set to the other are always in the same positive ratio Q_1/Q_2.*

It may seem that Postulate 5 is excessively complicated. However, it is easy to understand if it is compared with the theorem in affine geometry illustrated in Fig 3. Let two parallel lines and a fixed point O on one side of the parallel lines be given. Choose any pair of lines through O meeting the parallel lines as shown. Then the lengths *QS* and *PR* are always in the same positive ratio *QS/PR*.

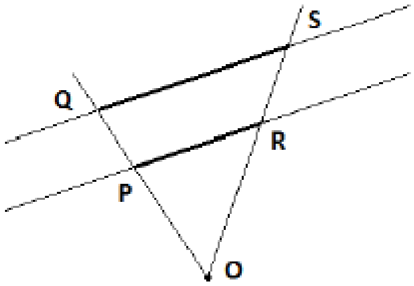

Figure 3. The ratio of lengths *QS*/*PR* is the same for all pairs of lines through O.

We now define thermodynamic **temperatures** T_1 and T_2 for the two environments by the equation

$$T_1/T_2 = Q_1/Q_2$$

with a standard value $T = 273.16$ K at the triple point of water. We also define **entropy** potentials S_1 and S_2 for the two isentropic sets so that

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

In what follows the word "temperature" will always mean "thermodynamic temperature", and the word "entropy" will always mean "entropy potential".

Example
At a pressure of one atmosphere an environment of melting ice has a temperature 273.15 K, and an environment of boiling water has a temperature 373.15 K.

Example
In air the temperature is $T = PV/R = E/2.5R$, where $R = 0.287$ kJ/(kg K), and the entropy is

$$S/R = 3.5 \ln(V/V_0) + 2.5 \ln(P/P_0),$$

where V_0 and P_0 specify the reference state with entropy potential zero.

Postulates 4 and 5, and the definitions of temperature and entropy, imply that the differential of the quasistatic heat on a quasistatic path is $dQ = TdS$, and the differential expression for the internal energy (Section 3.2) is

$$dE = TdS - PdV.$$

This shows that S is a function of V and E, in accordance with the state principle (Postulate 3), with $P = -(\partial E/\partial V)_S$ and $T = (\partial E/\partial S)_V$.

Example
The basic thermodynamic properties of one kilogram of air modeled as an ideal gas are shown on an E-V diagram in Fig 4. The isobars are sloping straight lines given by $E = 2.5PV$, the isotherms are horizontal straight lines given by $E = 2.5RT$, and the isentropic curves are given by

$$S/R = \ln(V/V_0) + \ln(E/E_0)^{2.5}.$$

The reference state for zero entropy is $V_0 = 1$ m^3/kg and $E_0 = 100$ kJ/kg.

Two more postulates are still required to say whether the entropy increases or decreases in an irreversible adiabatic change of state, and whether the temperature of a hotter state is greater than or less than that of a colder state.

Postulate 6. *Let S_1 and S_2 be the entropies of the isentropic sets Σ_1 and Σ_2 respectively. Then $S_1 < S_2$ if and only if $\Sigma_1 \rightarrow \Sigma_2$.*

It follows from this postulate that the quasistatic heat cannot be negative on any feasible quasistatic path in a system enclosed by thermally insulating walls.

Postulate 7. *Let T_1 and T_2 be the temperatures of the isothermal sets Θ_1 and Θ_2 respectively. Then $T_1 < T_2$ if and only if $\Theta_1 \rightarrow \Theta_2$.*

It follows from Postulates 6 and 7, and the definition of the *hotter* relation, that the quasistatic heat Q_{12} on a constant volume path from a state Z_1 to a state Z_2 is positive if and only if $T_1 < T_2$.

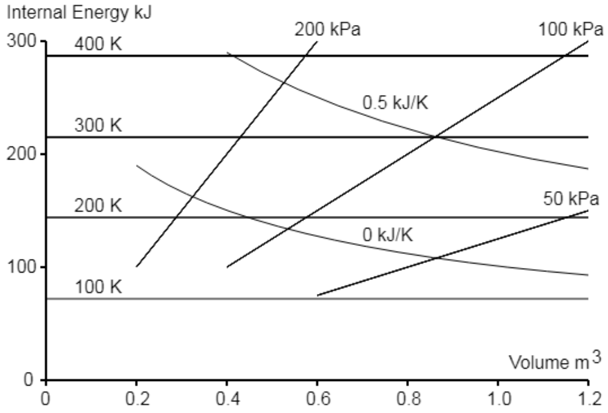

Figure 4. Properties of one kilogram of air modeled as an ideal gas.

3.4 The Second Part of the Second Law: The Principle of Increase of Entropy

Here we discuss the spontaneous changes of state that occur when a system is put in contact with an environment with which it is not initially in equilibrium. The environment is assumed to have a constant pressure P_e and a constant temperature T_e. Suppose the initial pressure of the system is P_i, the initial temperature is T_i, the final pressure is P_f, and the final temperature is T_f. There are four possible ways in which the walls of the container determine how the system is put in contact with the environment.

Fixed thermally insulating walls

In this case there is no mechanical or thermal contact with the environment and no change of state occurs.

Movable thermally insulating walls

If $P_i \neq P_e$ a spontaneous change in the volume of the system occurs until $P_f = P_e$.

Fixed thermally conducting walls

If $T_i \neq T_e$ a spontaneous change in the temperature of the system occurs until $T_f = T_e$.

Movable thermally conducting walls

In this case spontaneous changes in both the volume and the temperature of the system occur until $P_f = P_e$ and $T_f = T_e$.

It can be shown by arguments based on the foregoing definitions and postulates that in the last three spontaneous changes of state listed above the sum of the changes in the entropies of the system and the environment is positive. The proofs are rather long; details are given in my 2014 paper. These results lead to the following statement:

When a closed thermodynamic system which is not initially in equilibrium with its environment is put in mechanical or thermal contact with the environment a spontaneous change of state occurs in the system to a final state in equilibrium with the environment and the sum of the changes in the entropies of the system and the environment is positive.

The **Principle of Increase of Entropy** is a generalization of this result for all natural processes where coupled systems move spontaneously from states of disequilibrium towards states of mutual equilibrium and the total entropy of the coupled systems increases.

4. Concluding Remarks

This paper has presented only the basic concepts required in the new theory. It is possible to develop from them all the usual results given in conventional textbooks and the theory can be extended to other systems such as magnetic materials and electrochemical cells. My way of looking at thermodynamics may seem strange at first, but I hope that once you have grasped the ideas you will find them clear and easy to understand.

Bibliography

This is a list of the most important books and papers that have influenced my study of thermodynamics, plus two of my articles on the theory outlined in this paper.

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