

Multisystem temperature equilibration and the second law

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The entropy change during the temperature equilibration of an isolated collection of systems which may exchange heat (but not work) energy is shown to be positive. The proof holds when the constant volume heat capacity of each system is a non-negative function of the temperature. If the collection is allowed to exchange heat ΔQ with its environment during the equilibration, its entropy change ΔS is shown to satisfy the inequality $\Delta S \geq \Delta Q/T_f$, where T_f is the final equilibrium temperature. For infinitesimal equilibration transformations, this inequality reduces to a generalized statement of the second law of thermodynamics, showing that the internal portion of the entropy production during equilibration is non-negative.

I. INTRODUCTION

In classical thermodynamics courses, one normally encounters the second law of thermodynamics as a postulate, either in terms of the principle of entropy increase directly^{1,2} or via the well-known Clausius or Kelvin-Planck statements.³ Once established, the second law is used typically as a tool to predict certain behavioral aspects of macroscopic systems. For example, one standard example shows that heat flows from higher to lower temperatures and that the condition for thermal equilibrium is temperature equality.⁴ Similar applications of the second law can be found in regard to mechanical equilibrium and diffusion equilibrium.⁴ In another vein, one can study the limitations imposed upon the thermal efficiency of a heat engine by the principle of entropy increase.⁵

The present article entails an investigation of the second law from a different point of view. The goal here is not to use the second law to predict behavior, but rather to verify that one aspect of that law, namely, the principle of entropy increase, holds for a specific class of physical phenomena in isolated systems. This approach is believed to have potential pedagogical value since (a) it makes the second law less abstract and perhaps more credible to students, and (b) it provides a clear demonstration that the principle of entropy increase holds for a general class of physical phenomena, without appeal to specific numerical calculations involving heat transfers, specific heats and the like.

The material presented here was inspired by an article in this journal by Pyun⁶ in which it was demonstrated, using the properties of generalized means, that the entropy change accompanying the temperature equilibration of an isolated collection of systems in thermal contact is positive. One of the key assumptions made by Pyun was that each system's heat capacity was temperature independent. Of course, the second law of thermodynamics must hold even for the temperature equilibration of systems with temperature-dependent heat capacities. Unfortunately, the use of generalized means does not seem to be useful in the analysis of this more general case.

To the author's knowledge, all treatments of temperature equilibration in the traditional physics and chemistry literature, with the exception of Pyun's work,⁶ are confined to the special case of *two* systems in thermal contact and even here, the limitation of constant heat capacities is imposed. The specific goal in this article is to extend existing treatments of the temperature equilibration problem by

considering a collection of k thermally interacting systems, each of which has a non-negative, temperature-dependent heat capacity.⁷ Two distinct cases are dealt with in the following sections.

In Sec. II, it is shown that under the assumption that temperature equilibration occurs,⁸ the entropy of the collection increases if (a) the collection is energetically isolated from its environment, and (b) the individual systems in the collection may exchange heat energy, but each system maintains a constant volume and does zero work during the temperature equilibration. In Sec. III, condition (a) is relaxed to allow the exchange of heat energy between the collection and the environment, but condition (b) is retained. This leads to a derivation of a generalized statement of the second law for infinitesimal equilibration processes, showing that the internal portion of the entropy production during equilibration is non-negative.

II. ISOLATED COLLECTION WITH INTERNAL HEAT EXCHANGES

Consider k systems with initial absolute temperatures $T_i > 0$, $i = 1, 2, \dots, k$. These systems may exchange heat energy with one another, but each system is constrained to do zero work, and the collection as a whole is assumed to be energetically isolated from the remainder of the universe. During the temperature equilibration to the final temperature T_f , each system must obey the first law of thermodynamics. Specifically,

$$\Delta U_i = \Delta Q_i - \Delta W_i, \quad (1)$$

with

$$\Delta W_i = 0, \quad i = 1, 2, \dots, k. \quad (2)$$

Here, ΔU_i is the internal energy change, ΔQ_i is the heat gained, and ΔW_i is the work done by system i . The condition of isolation implies that

$$\Delta Q \equiv \sum_{i=1}^k \Delta Q_i = 0 \quad (3)$$

and

$$\Delta U \equiv \sum_{i=1}^k \Delta U_i = 0. \quad (4)$$

Of course, the first law of thermodynamics holds for the entire collection; i.e., $\Delta U = \Delta Q - \Delta W$, with each term

being identically zero. Note, however, that in contrast with (2) the terms ΔQ_i and ΔU_i are *not* constrained to be zero for all i .

During the actual temperature equilibration process, the collection can go through nonequilibrium states for which the temperature and other thermodynamic variables are not well defined. As is commonly done in thermodynamics, one can construct a quasistatic process connecting the initial and final states. This process can be used to calculate the entropy change, which depends only upon the initial and final states, and not upon the path connecting them. Such a path can be constructed, in principle, using external reversible heat and work sources.⁹ For the present case, since the systems each do zero work, it suffices to use only reversible heat sources (heat reservoirs). The quasistatic path will then be one of constant volume for each of the k systems, with each system gaining or losing sufficient heat to bring it to the final equilibrium temperature T_f .

Note that for all i , $\Delta W_i = 0$ for both the quasistatic path and the real process, and that ΔU_i is path independent because U_i is a state function. Therefore, it follows from Eqs. (1)–(4) applied to *both* processes that each ΔQ_i is also the same for both the quasistatic and the real processes. Thus, even though Q_i is *not* a state function in general, one can write here

$$\Delta Q = \sum_{i=1}^k \int_{T_i}^{T_f} C_{V,i}(T) dT = 0. \quad (5)$$

$C_{V,i}(T)$ is the temperature-dependent, constant-volume heat capacity for system i . The entropy change accompanying the equilibration for the collection is

$$\Delta S = \sum_{i=1}^k \int_{T_i}^{T_f} \frac{C_{V,i}(T)}{T} dT. \quad (6)$$

The primary goal in this section is to demonstrate that $\Delta S \geq 0$ under the constraint (5) for all $C_{V,i}(T) \geq 0$ for which the integrals in (5) and (6) are well defined, i.e., to show that the principle of entropy increase is satisfied. From a physical point of view this fundamental law *must* be satisfied. However, from a mathematical point of view the non-negativity of ΔS is not *a priori* obvious from (6) since the terms therein for which $T_i > T_f$ are negative. Furthermore, the implications of the constraint (5) are not immediately transparent.

The elegant mathematical treatment of Pyun⁶ makes use of the fact that when the heat capacities are all constant, the integrals in (5) and (6) can all be evaluated explicitly. Although such explicit evaluation is not possible for the present, more general case, the following argument proves the desired result in a way which is surprisingly elementary. It avoids entirely the somewhat sophisticated mathematical concepts of convexity and generalized means. In this regard, the proof here is more elementary than the one given previously for the special case with constant heat capacities.⁶

It is expedient to define the function

$$\Psi = \Delta Q - T_f \Delta S. \quad (7)$$

Owing to (5), Eq. (7) reduces to

$$\Psi = -T_f \Delta S. \quad (8)$$

Ψ is useful here because, in contrast with ΔS , which has both positive and negative terms, Ψ can be written as a sum of nonpositive terms. Specifically, the combination of (5)

and (6) allows (7) to be cast into the form

$$\Psi = \sum_{i=1}^k \int_{T_i}^{T_f} C_{V,i}(T) \left[1 - \left(\frac{T_f}{T} \right) \right] dT \leq 0. \quad (9)$$

The inequality follows from the fact that for each value of i , the summand is negative if $T_i \neq T_f$ and is zero if $T_i = T_f$. This is easily seen because: (a) if $T_i < T_f$, $1 - T_f/T \leq 0$ over the domain of the integral, and the sense of the integral is positive; (b) if $T_i > T_f$, $1 - T_f/T \geq 0$, but the sense of the integral is negative; (c) if $T_i = T_f$, the integral vanishes trivially. The equality in (9) holds if and only if $T_i = T_f$ for all i ; i.e., if no equilibration takes place.¹⁰

Combining (8) and (9), it follows immediately that

$$\Delta S \geq 0, \quad (10)$$

with the equality holding only for the trivial case when the k systems all have the same temperature initially. The above derivation of expression (10) is an explicit verification of the principle of entropy increase for the temperature equilibration of an arbitrary isolated collection of systems which may exchange heat but not work energy.

III. DIATHERMALLY ENCLOSED COLLECTION

Consider now a collection of k systems such as that in Sec. II, undergoing temperature equilibration. However, here the collection is allowed to exchange heat energy with its environment. Equations (1), (2), and (6) still apply, but (3)–(5) do not. The function Ψ defined by (7) still satisfies the inequality (9), even though (8) no longer holds. The combination of (9) and (7) implies

$$\Delta S \geq \Delta Q/T_f. \quad (11)$$

This provides a lower bound for the entropy change of the collection. This bound is positive if the collection gains heat ($\Delta Q > 0$) and is negative if the collection loses heat ($\Delta Q < 0$). The equality in (11) holds only if the initial k temperatures are all identical.

Explicit contact with the second law of thermodynamics can be made by considering the special case for which the k initial temperatures are very close to one another and the heat exchanged with the environment is very small. Under these conditions, the equilibration can be viewed, at least approximately, as being infinitesimal.

Then (11) becomes

$$dS \geq dQ/T_f. \quad (12)$$

This inequality is a generalized statement of the second law of thermodynamics. It holds when $dQ \neq 0$ and it reduces to the more familiar statement $dS \geq 0$ when $dQ = 0$. This generalized form of the second law is one of the fundamental postulates of irreversible thermodynamics.¹¹ Its meaning in the present context is that the entropy change for the collection can be written

$$dS = (dQ/T_f) + dS_{\text{int}}. \quad (13)$$

The first term on the right in (13) is the usual one for the infinitesimal exchange of heat with the collection as a whole. The second term is the internal entropy produced by the exchange of heat among the k systems within the collection during temperature equilibration. Expressions (12) and

(13) imply that

$$dS_{\text{int}} \geq 0. \quad (14)$$

This states that the internal entropy production is manifestly positive unless all k initial temperatures within the collection are identical. Then and only then, the internal entropy production is zero. The inequality (14) is equivalent to (12) and is another common way of writing the generalized form of the second law.¹¹

The statement of either (12) or (14) as a postulate in irreversible thermodynamics has an air of abstraction about it. The present derivation of these inequalities lends credence to that postulate and thus, can serve as a useful pedagogical tool, along with other examples which shed light on irreversible phenomena.¹²

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¹H. B. Callen, *Thermodynamics* (Wiley, New York, 1963), p. 24.

²H. Reiss, *Methods of Thermodynamics* (Blaisdell, Waltham, MA, 1965), Chap. IV.

³See, for example, D. ter Haar and H. N. S. Wergland, *Elements of Thermodynamics* (Addison-Wesley, Reading, MA, 1966), p. 17. See also Ref. 2, p. 70.

⁴See Ref. 1, Chap. 2.

⁵H. S. Leff and G. L. Jones, *Am. J. Phys.* **43**, 973 (1975).

⁶C. W. Pyun, *Am. J. Phys.* **42**, 896 (1974).

⁷For the systems treated here, it suffices to assume that the constant volume heat capacity C_V is non-negative. In contrast, using the second law directly, one can *prove* that C_V and its constant pressure counterpart C_P satisfy the relation $C_P \geq C_V \geq 0$. See L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1958), pp. 60-62.

⁸Throughout this paper, since the second law is not used explicitly, temperature equilibration is not predicted but, rather, is assumed. Given this, entropy increase during equilibration is then proved.

⁹Reference 1, p. 65.

¹⁰For the case where $C_{V,i}(T) = C_{V,i}(\text{const})$ for all i , Ψ can be evaluated, yielding $\Psi = \sum_i C_{V,i} [T_f - T_i - T_f \ln(T_f/T_i)]$. This is nonpositive, since $x - a - x \ln(x/a) < 0$ for $0 < x \neq a$, and is identically zero for $x = a$.

¹¹See, for example, S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), p. 21; P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley, New York, 1971), p. 14.

¹²One such example, which is related to the present discussion for $k = 2$, may be found in A. Katchalsky, *Nonequilibrium Thermodynamics in Biophysics* (Harvard U. P., Cambridge, MA, 1965), p. 44. Another example is provided in Ref. 5, where internal entropy production, in connection with irreversible Carnot cycles, is discussed.