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Connections between the Various Forms of the Second Law of Thermodynamics (*).

J. DUNNING-DAVIES

Department of Applied Mathematics, The University - Hull

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Summary. — The forms of the second law due to Carathéodory, Kelvin and Clausius are examined. The possible forms of thermodynamics which may be deduced from each of these statements are found before the connections between the separate forms of the law itself are examined. It is found that the usual proof of the equivalence of the Kelvin and Clausius statements is invalidated at negative absolute temperatures. However, it is shown that the Clausius statement is equivalent to the modified form of the Kelvin principle which is applicable for both positive and negative absolute temperatures.

1. – Introduction.

The second law of thermodynamics has been stated in various different ways. The three forms with which this article is concerned are:

a) Carathéodory's principle that all points A in thermodynamic phase space are i-points; that is, in every neighbourhood of every point A there are points adiabatically inaccessible from A.

b) Kelvin's principle that it is impossible to transform an amount of heat completely into work in a cyclic process in the absence of other effects.

c) Clausius' principle that it is impossible to transfer an amount of heat from a body to one warmer than itself in a cyclic process in the absence of other effects.

(*) To speed up publication, the author of this paper has agreed to not receive the proofs for correction.

Since these are all supposed to be statements of one law, it is desirable to know if they are equivalent and, if not, in what sense each of these forms implies the others.

In the following Sections, the connection between statements *a*) and *b*) and between statements *a*) and *c*) will be examined before the seemingly more straightforward case of the connection between the Kelvin and Clausius forms is considered.

2. – Types of thermodynamics.

By assuming the validity of the Kelvin or Carathéodory principles [1,2], an expression for the absolute temperature T in terms of the empirical temperature t may be found:

$$T = C \exp\left[\int_{t_0}^{t} g(t)\,\mathrm{d}t\right],$$

where C is an arbitrary constant and t_0 refers to a standard value of the empirical temperature.

If the further development of the subject is based on Carathéodory's principle, two choices arise at this point. First the choice of sign for the constant C. The second choice arises from the realization that an empirical temperature scale may be chosen so that heat tends to flow from places of high empirical temperature to those of low empirical temperature, or it flows in the reverse direction. These choices give rise to four possible types of thermodynamics, all similar in logical structure but distinct in detail [3].

Alternatively, if the further development is based on Kelvin's principle, the choice of sign for the constant C remains but the choice of direction of heat flow in terms of empirical temperatures does not remain. This follows since, if it is permissible for heat to flow from places of low empirical temperature to those of high empirical temperature, a process may be envisaged which violates Kelvin's principle: A process may be considered in which an amount of heat is partly converted into work, the remainder having passed from a hot reservoir to a cooler one. If it is possible to transfer heat from low to high temperatures, this quantity of heat may be returned to the hotter reservoir. The end result of these two processes is a violation of Kelvin's principle. Hence,

(1) M. W. ZEMANSKY: *Am. Journ. Phys.*, **34**, 914 (1966).

(2) P. T. LANDSBERG: *Thermodynamics with Quantum-Statistical Illustrations* (New York, 1961), p. 56.

(3) See P. T. LANDSBERG: *Thermodynamics with Quantum-Statistical Illustrations* (New York, 1961), p. 68.

the empirical temperature scale must be such that heat tends to flow from places of high empirical temperature to these of low empirical temperature.

It is seen, therefore, that a discussion based on the Kelvin statement of the second law leads to two types of thermodynamics. Those are the types I and II shown in Table I. The Carathéodory statement leads to all four possibilities and, by examining the Table, it may be noticed that Clausius' principle leads to thermodynamics of types I and IV. Further properties of the four types of thermodynamics are given by LANDSBERG (3).

TABLE I. – *Types of thermodynamics.*

Type	I	II	III	IV
Direction of heat flow in terms of empirical temperature	high → low	high → low	low → high	low → high
Sign of the absolute temperature (*i.e.* sign of C)	positive	negative	positive	negative
Direction of heat flow in terms of absolute temperature	high → low	low → high	low → high	high → low

3. – Connection between the principles of Carathéodory, Kelvin and Clausius.

It has been shown already that Kelvin's principle does imply the principle of Carathéodory (4) and the sense in which Carathéodory's principle implies that of Kelvin has been examined fully also (5). It remains to consider the connection between the Carathéodory and Clausius statements and that between the Kelvin and Clausius statements.

3·1. *Principles of Carathéodory and Clausius.* – As was seen in Sect. 2, Carathéodory's principle leads to the conclusion that either:

1) heat flows from places of high absolute temperature to those of low absolute temperature; or

2) heat flows from places of low absolute temperature to those of high absolute temperature.

Hence, to obtain Clausius' principle from Carathéodory's principle, it must be assumed that 1), rather than 2), holds. It is only in this sense that Clausius' principle may be deduced from Carathéodory's principle.

The problem of deducing the principle of Carathéodory from that of Clausius

(4) P. T. LANDSBERG: *Nature*, **201**, 485 (1964).
(5) J. DUNNING-DAVIES: *Nature*, **208**, 576 (1965).

must now be examined. Suppose phase space contains one point A which violates Carathéodory's principle; that is, the point A possesses a neighbourhood N, all points of which may be reached adiabatically from A. Also, suppose the point A lies on the isotherm of temperature T_1; as illustrated in the Figure. Let B be a second point on this isotherm, such that during the quasi-static isothermal process which takes A into B, the system gives up an amount of heat Q. The point B may then be linked with a point C, which lies on the isotherm of temperature T_2 $(T_2 > T_1)$, by a quasi-static adiabatic process. The point D which also lies on this second isotherm is chosen such that during the quasi-static isothermal process which takes C into D, the system absorbs an amount of heat Q. Since the points are assumed to lie within the neighbourhood N, it is possible to return from D to A by a quasi-static adiabatic process. Hence, in the cycle $ABCDA$, due to conservation of energy, the work done in stages two and four must cancel. Thus, the net result is the transfer of an amount of heat Q from a reservoir to one warmer than itself; contrary to Clausius' principle. It follows that points such as A cannot exist. Therefore, in every neighbourhood of every point C in thermodynamic phase space there are points adiabatically inaccessible from C.

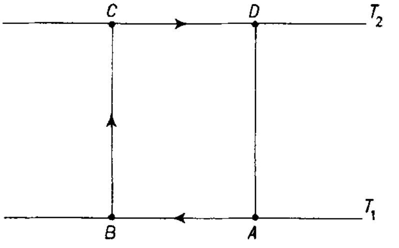

Fig. 1.

3·2. *Principles of Kelvin and Clausius.* – It is customary to regard these two forms of the second law of thermodynamics as being equivalent and a proof of this equivalence is given in some textbooks (6,7). However, from the preceding discussion, it is seen that this is not strictly so. The sense in which Carathéodory's principle implies that of Kelvin is different from the sense in which it implies the Clausius statement. The proof of the equivalence of these two statements is invalidated only at negative absolute temperatures, as has been pointed out before (8).

The modified form of the Kelvin principle which is applicable for both positive and negative absolute temperatures states that in a cyclic process, in the absence of other effects, heat cannot be converted completely into work for states of positive absolute temperature and work cannot be converted completely into heat for states of negative absolute temperature. It is now neces-

(6) M. W. Zemansky: *Heat and Thermodynamics* (New York, 1957).

(7) See P. T. Landsberg: *Thermodynamics with Quantum-Statistical Illustrations* (New York, 1961), p. 177.

(8) J. G. Powles: *Contemp. Phys.*, **4**, 338 (1963).

sary to consider the connection between this modified Kelvin principle and the Clausius principle.

As has been pointed out (9), it might be thought possible to violate the Clausius principle by constructing a machine which would extract heat from a reservoir and convert it into work without other effects. This work could then be converted into heat which is transferred to a hotter reservoir. This would violate the Clausius principle. However, from the modified Kelvin principle, it is seen that, at positive absolute temperatures, the first step in this process is impossible and, at negative absolute temperatures, the second step cannot be achieved. Hence, the modified Kelvin statement does imply the Clausius statement.

It is known already that, for positive absolute temperatures, Clausius' principle does imply the modified Kelvin principle (6,7). For the case of negative absolute temperatures, suppose the modified Kelvin principle is false, and construct a machine *M* which can convert an amount of work completely into heat in the absence of other effects. Also consider the process in which heat is transferred from one body to a warmer body, this being achieved by the production of work. By using the machine *M*, this work may be converted completely into heat. The end result of this two-step process is that heat has been transferred from a body to one warmer than itself in the absence of other effects. This violates Clausius' principle. Hence, the Clausius statement does imply the modified form of the Kelvin postulate.

Therefore, although the original principles of Kelvin and Clausius are equivalent for positive absolute temperatures only, the modified Kelvin principle and the original Clausius statement are equivalent for both positive and negative absolute temperatures.

(9) N. F. Ramsey: *Phys. Rev.*, **103**, 20 (1956), and papers cited there.

RIASSUNTO (*)

Si esaminano le forme della seconda legge dovute a Carathéodory, Kelvin e Clausius. Si trovano le forme possibili di termodinamica che si possono dedurre da ognuna di esse prima di esaminare le connessioni fra le diverse forme della legge stessa. Si trova che la solita dimostrazione dell'equivalenza delle formulazioni di Kelvin e Clausius non è più valida per temperature assolute negative. Si dimostra che l'enunciato di Clausius è equivalente alla forma modificata del principio di Kelvin che è applicabile a temperature assolute sia positive che negative.

(*) *Traduzione a cura della Redazione.*

Соотношения между различными формами второго закона термодинамики.

Резюме (*). — Изучаются формы второго закона термодинамики, разработанные Каратеодори, Кельвиным и Клаузиусом. Определяются возможные формы термодинамики, которые могут быть выведены из каждого из этих утверждений, перед тем как исследовать соотношения между отдельными формами самого закона. Обнаружено, что обычное доказательство эквивалентности утверждений Кельвина и Клаузиуса не справедливо при отрицательных абсолютных температурах. Однако, показывается, что фориулировка Клаузиуса эквивалентна модифицированной форме принципа Кельвина, который применим и для положительных и для отрицательных абсолютных температур.

(*) *Переведено редакцией.*