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Mathematical formulation of the heat-engine theory of thermodynamics including negative absolute temperatures

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Abstract. In order to treat negative absolute temperatures in the heat-engine theory of thermodynamics with logical consistency, a mathematical scheme is proposed which consists of three basic concepts, *cycles*, *reservoirs* and *heats*, and three axioms (1) the existence of at least one irreversible cycle, (2) the existence of a reversible cycle operating between any two reservoirs, (3) the scaling of the size of a cycle and the combination of two cycles. The axiom (1) is the weakest form of the second law of thermodynamics. A basic theorem of the heat-engine theory, a stronger version of Carnot's theorem, is derived, and based on it the meaning of temperature is clarified and various forms of the second law are investigated to examine the possibility of negative absolute temperatures. The set of cycles is represented as a half-space in a vector space, and the absolute temperatures are related to a normal vector of the hyperplane which supports the half-space.

1. Introduction

In this paper we give a logically consistent formulation of the heat-engine theory of thermodynamics including negative absolute temperatures.

The idea of negative absolute temperatures was proposed by Purcell and Pound (1951), Landau and Lifshitz (1951) and Ramsey (1956) in connection with the statistical mechanics of nuclear spin systems. Since then many attempts have been made to introduce negative absolute temperatures consistently into thermodynamics, and various reformulations of the second law of thermodynamics have been proposed (Landsberg 1959, 1977, Schöpf 1962, Powles 1963, Marvan 1966, Tykodi 1975, 1976, 1978, Tremblay 1976, Danielian 1976, White 1976, Dunning-Davies 1976, 1978)†. However, in these attempts, the concept of absolute temperatures is treated as being given prior to the second law, and the heat-engine theoretical construction of thermodynamics with negative absolute temperatures has not been completed. The difficulty in the heat-engine theoretical treatment of negative absolute temperatures is, as explained below, due to the loose definition of absolute temperatures in the conventional heat-engine theory.

The conventional heat-engine theory is constructed by the following four steps: (i) The Carnot theorem (all reversible engines operating between two fixed temperatures have the same efficiency) is derived from the first and the second laws of thermodynamics. (ii) The absolute temperatures are defined, based on the Carnot theorem, as $T_1/T_2 = -Q_1/Q_2$ (Q_1 and Q_2 are the heats *drawn from* two reservoirs by a reversible

† The best real example, namely the laser, has been explored to a great extent from the quantum statistical point of view, and we have recently discussed it in its thermodynamic connection (Hasegawa and Nakagomi 1979).

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engine). (iii) The Clausius inequality ($\Sigma_i Q_i T_i^{-1} \leq 0$) is established for a cycle operating between many reservoirs based on the steps (i) and (ii). (iv) By introducing states of a thermodynamic system, the quantity *entropy* is defined for each state and the principle of the increase of entropy in adiabatic processes is derived from the Clausius inequality.

As can be seen in step (ii), the sign of absolute temperatures is indefinite. If we take the Kelvin–Planck formulation of the second law, we get the result that all absolute temperatures (defined in (ii)) must have the same sign. It is usual to adopt the positive sign, but there is no absolute reason for this convention. The Clausius inequality is, however, due to this adoption of the positive sign (if the opposite sign is adopted, the inequality must be reversed). Thus, in order to include negative absolute temperatures in the heat-engine theory, it is necessary to impose a further condition to characterise the sign of absolute temperatures upon their definition in step (ii) as well as to replace the Kelvin–Planck formulation of the second law by a more suitable one. It is desirable to demand, as this condition, that the Clausius inequality should be satisfied, because then the principle of the increase of entropy is guaranteed for negative absolute temperatures as well as positive (Landsberg's analysis (1977) is essentially based on this demand). Unfortunately, however, step (iii) comes after step (ii) in the conventional framework, hence the Clausius inequality cannot be used in the definition of absolute temperatures. This is the crucial point, if one desires a satisfactory heat-engine theory, which has not been worked out.

In this paper we solve the above dilemma by establishing the following statement before introducing absolute temperatures: *There exists a quantity g_i for each reservoir i such that $\Sigma_i Q_i g_i \geq 0$ and the quantities g_i are unique up to a common positive factor.* The absolute temperatures of reservoirs T_i that are defined so as to satisfy the Clausius inequality are then given by $T_i = -\alpha g_i^{-1}$ ($\alpha > 0$), and the steps (i), (ii), (iii) are condensed in this statement, which is the fundamental theorem in this paper. Our derivation of this theorem is based on three axioms: (1) there exists at least one irreversible cycle; (2) for any two reservoirs there exists a reversible cycle operating between them; (3) one can scale the size of a cycle and combine two cycles. Since all of the formulations of the second law in the heat-engine theory imply the axiom (1), it can be regarded as the weakest form of the second law. Note that the assumptions corresponding to axioms (2) and (3) are tacitly used in the conventional heat-engine theory. Since the problem under consideration is logically delicate, a clear mathematical formulation is desirable. In § 2, we give mathematical expressions for the three axioms and the fundamental theorem, where the terms *cycles, heats* and *reservoirs* are all ingredients of the present formulation.

The fundamental theorem has a simple geometrical interpretation; especially in the two-reservoir case, it can be visualised on the plane $\boldsymbol{R}^2$. Let us call a vector (x_1, x_2) an allowed vector if we can choose a cycle whose heats drawn from the reservoirs 1 and 2 are x_1 and x_2 respectively. Then the axiom (1) gives an allowed vector $\boldsymbol{a}$ such that $-\boldsymbol{a}$ is not allowed, the axiom (2) gives two allowed vectors $\boldsymbol{b}$ and $-\boldsymbol{b}$, and the axiom (3) states that the vectors $\alpha\boldsymbol{a} + \beta\boldsymbol{b}(\alpha \geq 0, -\infty < \beta < +\infty)$ are all allowed. Thus the set of all allowed vectors occupies a half-plane in $\boldsymbol{R}^2$ (see figure 1). This is the assertion of the fundamental theorem illustrated for the two-reservoir case. The vector $\boldsymbol{g} = (g_1, g_2) = -(T_1^{-1}, T_2^{-1})$ is the normal vector of the line supporting the half-plane. Also, it can be shown that various formulations of the second law are reflected in the restriction on the direction of the normal vector $\boldsymbol{g}$. The proof of the fundamental theorem (§ 3) is suggested by this geometrical interpretation which is adaptable in many-reservoir cases (even in the case of uncountably infinite reservoirs).

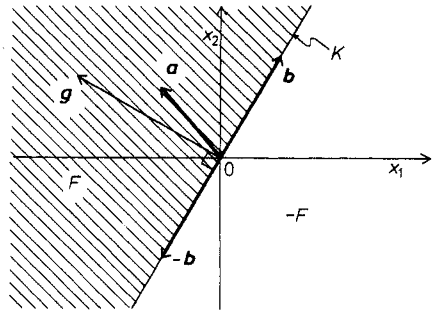

Figure 1. Illustration in the two-reservoir case. The vectors $\boldsymbol{b}$ and $-\boldsymbol{b}$ correspond to a reversible cycle and its reversed cycle, and the vector $\boldsymbol{a}$ to an irreversible cycle. Any possible cycle is represented by a vector in the hatched region F; in particular, the boundary K represents the set of reversible cycles.

In § 4, the concept of temperature is first introduced as the hotter–colder relation between reservoirs, and then the connection between this hotter–colder relation and absolute temperatures is fixed based on the fundamental theorem. In § 5, the Clausius and the Kelvin–Planck forms of the second law and their modifications are re-examined in our framework, and the range of possible absolute temperatures is given for each form of the second law. In § 6, the axiom (2) is somewhat weakened so as to fit real situations. The discussion of the step (iv) of the heat-engine theory needs further preparations, and is not included in the present work.

Besides the logically consistent treatment of negative absolute temperatures, our formulation of the heat-engine theory has the following advantages: (a) Our formulation includes no tacit assumptions except the three axioms. (b) Any concept concerning temperature such as hotter or colder, empirical temperature, or the zeroth law (Home 1977, Bergthorsson 1977) is not included in the axioms. (c) The first law is not used (the necessity of the first law depends upon the way to formulate the second law, e.g., it is necessary in the case of the Kelvin–Planck formulation, and not in the case of the Clausius formulation). (d) It is derived naturally that ± 0 are not included in the range of possible absolute temperatures (this is consistent with the third law), and $+\infty$ and $-\infty$ of absolute temperatures that can be included are the same temperature.

2. Mathematical formulation

The object of our mathematical study is the system† that consists of two non-empty sets Θ and $\mathscr{C}$ and a mapping Q of $\mathscr{C}$ into $\boldsymbol{R}_0^{\Theta} \equiv \{x = (x_\theta;\ \theta \in \Theta);\ x_\theta \in \boldsymbol{R}\ \forall \theta \in \Theta,\ x_\theta = 0$ except

† The physical meaning of the system $\{\Theta, \mathscr{C}, Q\}$ is as follows: Θ is a set of heat reservoirs, and a cycle c means a device periodically operating between several reservoirs in Θ which will produce no effect except the exchanging of heat with the reservoirs and the doing of work. $\mathscr{C}$ is the set of all possible cycles, and the three axioms provide the conditions for the possible cycles. The choice of the axioms is reasonable as explained briefly in § 1. The quantity $Q_\theta(c)$ is the amount of heat drawn from the reservoir θ in a cyclic process by the cycle c. The set Θ may be infinite, but we deal with only such cycles as make contact with a *finite* set of reservoirs (i.e. $Q(c) \in \boldsymbol{R}_0^{\Theta}$) because the axioms are obtained on the basis of the experience for such cycles. In particular, the cycles which make contact with only two reservoirs θ and θ' are contained in $\mathscr{C}(\theta, \theta')$. It is noted that cycles are not necessarily represented as cyclic paths in thermostatic phase spaces of the working substances, and that we do not use the concept of (equilibrium) states.

for a finite set of θ}, where $\boldsymbol{R}$ is the real line and $\boldsymbol{R}_0^\Theta$ is a vector space with the operations $x+y\equiv(x_\theta+y_\theta)$ and $\alpha x\equiv(\alpha x_\theta)$ ($\alpha\in\boldsymbol{R}$). The elements $\theta\in\Theta$ and $c\in\mathscr{C}$ are called reservoirs and cycles respectively and the θ component $Q_\theta(c)$ of $Q(c)=(Q_\theta(c))$ is called the θ-heat of the cycle c. The mathematical structure of the system $\{\Theta, \mathscr{C}, Q\}$ is provided by the three axioms given below.

Definition 2.1. A cycle c is called *reversible* if there exists a cycle c' such that $Q(c')=-Q(c)$, otherwise *irreversible.* A cycle c is called a *zero* cycle if $Q(c)=0$, otherwise a *non-zero* cycle.

Definition 2.2. For any two reservoirs θ and θ' a set $\mathscr{C}(\theta, \theta')$ is defined as

$$\mathscr{C}(\theta, \theta')\equiv\{c\in\mathscr{C};\, Q_{\theta''}(c)=0 \qquad \text{if } \theta''\neq\theta \text{ and } \theta''\neq\theta'\}.$$

Axiom 1. There exists at least one irreversible cycle.
Axiom 2. For any pair of reservoirs θ and θ' ($\theta\neq\theta'$), there exists at least one non-zero reversible cycle in $\mathscr{C}(\theta, \theta')$.
Axiom 3. For any two cycles c and c' and for any non-negative numbers α and β, there exists a cycle c'' such that $Q(c'')=\alpha Q(c)+\beta Q(c')$.

Axioms 1, 2, 3 are the mathematical refinements of the axioms (1), (2), (3) mentioned in the Introduction.

Theorem 2.1. If axioms 1, 2, 3 are all satisfied, then there exists a mapping g of Θ into $\boldsymbol{R}$ such that

$$\left\{x=(x_\theta)\in\boldsymbol{R}_0^\Theta;\, \sum_\theta g(\theta)x_\theta\geqslant 0\right\}=\{Q(c);\, c\in\mathscr{C}\} \tag{2.1}$$

and the mapping g is unique up to a positive multiplicative constant. Conversely, if there exists a mapping g of Θ into $\boldsymbol{R}$ satisfying the condition (2.1), then axioms 1, 2 and 3 hold.

Theorem 2.1 is the fundamental theorem announced in the Introduction. The proof of this theorem is given in the next section.

3. Proof of Theorem 2.1 and geometrical representation

The proof of theorem 2.1 is given by translating axioms 1, 2, 3 into the statements in the vector space $\boldsymbol{R}_0^\Theta$. Let us define the following notations: $F=\{Q(c);\, c\in\mathscr{C}\}$, $D(x)=\{\theta\in\Theta;\, x_\theta\neq 0\}$ ($x\in\boldsymbol{R}_0^\Theta$), and $n(x)=$ *the number of elements in* $D(x)$. Then axioms 1, 2, 3 are represented in $\boldsymbol{R}_0^\Theta$ as follows, respectively:
P1. $F\backslash K\neq\phi$, where $K=F\cap(-F)$ and $-F=\{-x;\, x\in F\}$.
P2. For any θ, $\theta'\in\Theta$ ($\theta\neq\theta'$), there exists $x\in K$ such that $\phi\neq D(x)\subset\{\theta, \theta'\}$.
P3. If $x, x'\in F$, $\alpha\geqslant 0$, and $\beta\geqslant 0$, then $\alpha x+\beta x'\in F$.
From the above three properties, we get a series of lemmas.

Lemma 1. K is a subspace in $\boldsymbol{R}_0^\Theta$.
Proof. It is obvious from the property *P3* and the definition of K. □

Lemma 2. There exists $\hat{x}\in F\backslash K$ such that $n(\hat{x})=1$.
Proof. From the property *P1*, we see that $0\notin F\backslash K\neq\phi$; then the minimum number r of

$n(x)$ for $x \in F\backslash K$ is a positive integer. Let us assume $r \geqslant 2$, then there exist $z \in F\backslash K$ and $\theta, \theta' \in \Theta (\theta \neq \theta')$ such that $n(z) = r$ and $D(z) \supset \{\theta, \theta'\}$. By the property *P2*, there exists $w \in K$ such that $\phi \neq D(w) \subset \{\theta, \theta'\}$, then we can choose a suitable number $\alpha \in R$ such that $z_\theta + \alpha w_\theta = 0$ or $z_{\theta'} + \alpha w_{\theta'} = 0$. This means that $n(z + \alpha w) < r$. Moreover it is obvious that $z + \alpha w \in F\backslash K$, because $z + \alpha w \in K$ implies $z \in K$. The result is contradictory to the definition of r. Therefore, we have $r = 1$. □

Lemma 3. Let $\hat{x}$ be an element in $F\backslash K$ such that $n(\hat{x}) = 1$ (the existence of such an element is guaranteed by lemma 2). Then any $x \in F$ can be expressed as follows:

$$x = \alpha \hat{x} + w \qquad \text{with } \alpha \geqslant 0 \text{ and } w \in K. \tag{3.1}$$

Proof. Put $D(\hat{x}) = \{\theta_0\}$ and take any $x \in F$. If $D(x) \subset \{\theta_0\}$, then x is obviously written in the form (3.1). In the other case (i.e., $D(x)\backslash\{\theta_0\} \neq \phi$), the proof is as follows: From *P2*, for each $\theta \in D(x)\backslash\{\theta_0\}$ there exists $y^\theta \in K$ such that $\phi \neq D(y^\theta) \subset \{\theta, \theta_0\}$. If $\theta \notin D(y^\theta)$ then $\hat{x} = (x_{\theta_0}/y^\theta_{\theta_0}) y^\theta \in K$, which is contradictory to $\hat{x} \in F\backslash K$. Therefore, $\theta \in D(y^\theta)$. Then we can define $z \in F$ by

$$z = \sum_{\theta \in D(x)} \beta_\theta y^\theta + x \qquad \text{with } \beta_\theta = -x_\theta / y^\theta_\theta.$$

It is obvious that $z_\theta = 0$ for $\theta \neq \theta_0$, hence $z = \alpha \hat{x}$ $(\alpha = z_{\theta_0}/\hat{x}_{\theta_0})$. Therefore, $x = \alpha \hat{x} + w$ where $w = -\Sigma_\theta \beta_\theta y^\theta \in K$. If $\alpha < 0$, then $-\hat{x} = -\alpha^{-1} z \in F$, i.e., $\hat{x} \in K$, which is contradictory to $\hat{x} \in F\backslash K$. Therefore, we get $\alpha \geqslant 0$. □

Lemma 4. For any $\theta \in \Theta$, there exists $x \in F$ such that $D(x) = \{\theta\}$.
Proof. Assume $\hat{x}$ and θ_0 as in the proof of lemma 3, i.e., $\hat{x} \in F\backslash K$, $D(\hat{x}) = \{\theta_0\}$. If $\theta \neq \theta_0$ then by the property *P2* there exists $z \in K$ such that $\phi \neq D(z) \subset \{\theta, \theta_0\}$. If $\theta_0 \notin D(z)$, then $D(z) = \{\theta\}$ and $z \in F$. If $\theta_0 \in D(z)$, then $D(x) = \{\theta\}$ and $x \in F$ where $x = \alpha z + \hat{x}$ $(\alpha = -\hat{x}_{\theta_0}/z_{\theta_0})$. □

Lemma 5. K is a hyperplane† in $\boldsymbol{R}^\Theta_0$ containing the zero vector.
Proof. From lemma 3 and the property *P3*

$$F = [\hat{x}]^+ + K \tag{3.2}$$

where $[\hat{x}]^+ = \{\alpha \hat{x}; \alpha \geqslant 0\}$ and $A + B = \{x + y; x \in A, y \in B\}$ for $A, B \subset \boldsymbol{R}^\Theta_0$. Then

$$F \cup (-F) = [\hat{x}] + K \tag{3.3}$$

where $[\hat{x}] = \{\alpha \hat{x}; \alpha \in \boldsymbol{R}\}$. On the other hand, by lemma 4, for any $\theta \in \Theta$ there exists $x^\theta \in F$ such that $D(x^\theta) = \{\theta\}$. Hence, the algebraic basis $\{e^\theta; \theta \in \Theta\}$ of the vector space $\boldsymbol{R}^\Theta_0$ (defined by $D(e^\theta) = \{\theta\}$ and $e^\theta_\theta = 1$) is contained in $F \cup (-F)$, because $e^\theta = (1/x^\theta_\theta) x^\theta \in F$ or $\in (-F)$. Then from lemma 1 and equation (3.3) we see that $[\hat{x}] + K$ is a subspace containing the basis $\{e^\theta; \theta \in \Theta\}$, therefore $[\hat{x}] + K = \boldsymbol{R}^\Theta_0$. □

Here we use the following well known general lemma.

Lemma 6. If H is a hyperplane in a vector space L containing the zero vector, then there exists a linear functional f on L such that

$$H = \{x \in L; f(x) = 0\},$$

† In general, a subspace H in a vector space L is called a hyperplane containing the zero vector if there exists a one-dimensional subspace V such that $V + H = L$.

and f is unique up to a non-zero multiplicative constant. For the proof of lemma 6, see Valentine (1964).

Proof of Theorem 2.1. By lemmas 5 and 6, there exists a linear functional f on $\boldsymbol{R}_0^\theta$ such that

$$K=\{x\in\boldsymbol{R}_0^\Theta\,;f(x)=0\} \tag{3.4}$$

and the functional f is unique up to a non-zero multiplicative constant. Then from lemma 3 or the relation (3.2) we have

$$F=\{x\in\boldsymbol{R}_0^\Theta\,;f(x)\geqslant 0\}\quad(\text{or }=\{x\in\boldsymbol{R}_0^\Theta\,;f(x)\leqslant 0\}).$$

Therefore, by putting $g(\theta)=f(e^\theta)\forall\theta\in\Theta$ (or $g(\theta)=-f(e^\theta)\forall\theta\in\Theta$) ($e^\theta$ are defined in the proof of lemma 5, i.e., $D(e^\theta)=\{\theta\}$ and $e_\theta^\theta=1$), we get the relation (2.1).

If a mapping $g:\Theta\to\boldsymbol{R}$ satisfies (2.1), then the linear functional defined by $f(x)=\Sigma_\theta\, g(\theta)x_\theta$ satisfies (3.4). Therefore, the mapping g is unique up to a scaling factor, moreover, the scaling factor must be positive in order to conserve the inequality in (2.1).

The latter half of theorem 2.1 is easily checked. □

4. Temperatures

The concept of *temperature* is primarily defined by a *hotter–colder relation.*

Definition 4.1. We define a relation $\lesssim$ in Θ (called temperature order) as

$$\theta'\lesssim\theta \Leftrightarrow \begin{cases}\theta'=\theta\\ \quad\text{or}\\ \theta'\neq\theta\text{ and }\exists x\in\mathscr{C}\text{ such that }-Q_{\theta'}(c)=Q_\theta(c)>0\end{cases}$$

and related notations $\approx$ and $<$ are defined as

$$\theta'\approx\theta \Leftrightarrow \theta'\lesssim\theta\text{ and }\theta\lesssim\theta',$$

$$\theta<\theta' \Leftrightarrow \text{the relation }\theta'\lesssim\theta\text{ is not true.}$$

The physical meaning of the relation $\theta'\lesssim\theta$ is that the reservoir θ' is not hotter than the reservoir θ, and consequently, $\theta<\theta'$ means that θ' is hotter than θ, and $\theta'\approx\theta$ means that the two reservoirs θ' and θ are in thermal equilibrium with each other.

From theorem 2.1 we can observe the fact that

$$\theta'\lesssim\theta \Leftrightarrow g(\theta')\leqslant g(\theta). \tag{4.1}$$

From this fact we see that the mapping g serves as the measure of the temperature order, and that the relation $\lesssim$ is a total quasi-order in Θ i.e., (i) $\theta\lesssim\theta$, (ii) $\theta\lesssim\theta'$ and $\theta'\lesssim\theta''\Rightarrow\theta\lesssim\theta''$, (iii) for any $\theta,\theta'\in\Theta$, $\theta\lesssim\theta'$ or $\theta'\lesssim\theta$ holds. The property (ii) is the transitivity, which is the essential feature of temperature (Home 1977, Bergthorsson 1977).

Definition 4.2. The absolute temperature $T(\theta)$ specified to each reservoir θ is defined by a mapping $T:\Theta\to\{x;\,-\infty\leqslant x<0 \text{ or } 0<x\leqslant+\infty\}$ such that

$$\sum_{\theta} T(\theta)^{-1}Q_\theta(c)\leqslant 0 \qquad \forall c\in\mathscr{C} \tag{4.2}$$

with equality iff c is reversible, where $(\pm\infty)^{-1}=0$.

From theorem 2.1 we get the relation

$$T(\theta)=\begin{cases}-\alpha g(\theta)^{-1} & \text{if } g(\theta)\neq 0\\ +\infty \text{ or } -\infty & \text{if } g(\theta)=0\end{cases} \tag{4.3}$$

where α is a positive constant. From this relation we have the following facts:

(a) $T(\theta)=T(\theta')\Rightarrow\theta\approx\theta'$

(b) $T(\theta)=+\infty$ and $T(\theta')=-\infty\Rightarrow\theta\approx\theta'$

(c) $T(\theta)>0$, $T(\theta')=+\infty$ or $-\infty$, and $T(\theta'')<0\Rightarrow\theta<\theta'<\theta''$

(d) $0<T(\theta)<T(\theta')\Rightarrow\theta<\theta'$

(e) $T(\theta)<T(\theta')<0\Rightarrow\theta<\theta'$.

It is noted that in our scheme the coldest or the hottest reservoirs of all possible reservoirs do not exist, in other words, the reservoirs with absolute temperatures $T=\pm 0$ do not exist. This is consistent with the third law of thermodynamics (e.g. ter Haar and Wergeland 1966). If we use the mapping g as a temperature scale, these extreme temperatures correspond to $g=\pm\infty$, which are naturally excluded; moreover, the temperature order $\leqslant$ is represented faithfully by g (c.f. (4.1)) and not by T. It is then theoretically preferable to use g rather than T as a temperature-scale.

5. Various forms of the second law

We will set forth various forms of the second law and inquire their relation with our axioms and the resultant restrictions on the range of possible absolute temperatures.

Definition 5.1. A mapping $W:\mathscr{C}\to\boldsymbol{R}$ (called *work*) is defined by $W(c)=\Sigma_\theta Q_\theta(c)$. A cycle c is called a *non-work* cycle if $W(c)=0$.

Original Clausius form (OC). There exists a total quasi-order $\leqslant$ in Θ such that if $\theta\not\leqslant\theta'$ then $Q_\theta(c)>0$ for any non-zero and non-work cycle $c\in\mathscr{C}(\theta,\theta')$, and there exists at least one pair $\theta,\theta'\in\Theta$ such that $\theta\not\leqslant\theta'$.

Weak Clausius form (WC). For some two reservoirs θ and $\theta'\in\Theta$, the θ-heat $Q_\theta(c)$ is positive for any non-zero and non-work cycle $c\in\mathscr{C}(\theta,\theta')$.

Original Kelvin–Planck form (OKP). For *any* $\theta\in\Theta$, all non-zero cycles $c\in\mathscr{C}(\theta)$ have negative work, $W(c)<0$, where $\mathscr{C}(\theta)=\mathscr{C}(\theta,\theta)$.

Weak Kelvin–Planck form 1 (WKP–1). For *any* $\theta\in\Theta$, all non-zero cycles $c\in\mathscr{C}(\theta)$ are irreversible.

Weak Kelvin–Planck form 2 (WKP–2). For *some* $\theta\in\Theta$, all non-zero cycles $c\in\mathscr{C}(\theta)$ are irreversible.

Anti-Kelvin-Planck form (AKP). For *any* $\theta \in \Theta$, all non-zero cycles $c \in \mathscr{C}(\theta)$ have positive work, $W(c) > 0$.

Since any one of the above statements OC, ..., AKP implies axiom 1, the combination of axioms 2 and 3 with any one of OC, ..., AKP implies the existence of the mapping g satisfying the condition (2.1), but the converse proposition (like the latter half of theorem 2.1) is not necessarily true. Further but easy investigations reveal the following facts.†

$$\text{(f)} \quad (\text{WKP–2, A2, A3}) \Leftrightarrow (\text{A1, A2, A3}) \Leftrightarrow \exists g G(g)$$

where $G(g)$ represents the statement that the mapping g satisfies the condition (2.1), and A1, A2, A3 are abbreviations of axioms 1, 2, 3 respectively.

$$\text{(g)} \quad (\text{OC, A2, A3}) \Leftrightarrow (\text{WC, A2, A3}) \Leftrightarrow \exists g(G(g), \exists \theta, \theta' \in \Theta \qquad g(\theta) \neq g(\theta'))$$

$$\text{(h)} \quad (\text{OKP, A2, A3}) \Leftrightarrow \exists g(G(g), \qquad g < 0)$$

$$\text{(i)} \quad (\text{WKP–1, A2, A3}) \Leftrightarrow \exists g(G(g), \qquad g \neq 0)$$

$$\text{(j)} \quad (\text{AKP, A2, A3}) \Leftrightarrow \exists g(G(g), \qquad g > 0).$$

Thus, by referring to the relation (4.3), we can see that the absolute temperature T is restricted to positive values for OKP, to finite values for WKP–1, and to negative value for AKP. The Clausius forms OC and WC do not restrict the range of T but require the existence of two reservoirs which are not in thermal equilibrium with each other. Only WKP–2 is equivalent to axiom 1 under axioms 2 and 3.

6. Modification of axiom 2

The reversible cycle is an ideal concept, so that it is desirable to weaken axiom 2.
Axiom 2'. For any pair $\theta, \theta' \in \Theta$ $(\theta \neq \theta')$ and any $\epsilon > 0$, there exist non-zero cycles c and $c' \in \mathscr{C}(\theta, \theta')$ such that

$$|Q_\theta(c) + Q_\theta(c')| + |Q_{\theta'}(c) + Q_{\theta'}(c')| < \epsilon\{|Q_\theta(c) + Q_{\theta'}(c)|\}.$$

Axiom 2' asserts the existence of asymptotically reversible cycles. Theorem 2.1 is modified as follows:

Theorem 6.1. If axioms 1, 2', 3 are all satisfied, then there exists a mapping g of Θ into $\boldsymbol{R}$ such that

$$\left\{x \in \boldsymbol{R}_0^\Theta; \sum_\theta g(\theta) x_\theta > 0\right\} = \{Q(c); c \in \mathscr{C}_\mathrm{i}\} \tag{6.1}$$

where $\mathscr{C}_\mathrm{i}$ is the set of all irreversible cycles. The mapping g is unique up to a positive multiplicative constant. Conversely, if there exists a mapping g satisfying (6.1) then axioms 1, 2' and 3 hold.
Proof. Define $F_0 = \{Q(c); c \in \mathscr{C}\}$ and

$$F = F_0 \cup \{x \in \boldsymbol{R}_0^\Theta; \exists y \in F_0, \forall \epsilon > 0 \; x + \epsilon y \in F_0 \; x - \epsilon y \in (-F_0)\}.$$

It is easily checked that the set F has the properties *P1, P2, P3* stated in the beginning of § 3; hence, one can prove the theorem by using the discussion in § 3. □

† Here, the notation $(X, Y, \ldots)$ for the statements $X, Y, \ldots$ means 'X and Y and ...'.

$(f), \ldots, (j)$ in § 5 hold by the conversions of axiom 2 with axiom 2′ and of $G(g)$ with $G'(g)$, where $G'(g)$ means the statement that the mapping g satisfies the condition (6.1).

7. Concluding remarks

The validity of the axioms adopted here as a basis of thermodynamics depends upon experiments and the interpretation of $\mathscr{C}$, Θ and $Q_\theta(c)$. However, the mathematical part of the discussion in this paper is independent of the interpretations of $\mathscr{C}$, Θ and $Q_\theta(c)$, and so it can be applied to any system which satisfies axioms 1, 2, 3 or their modifications in §§ 5 and 6 with another interpretation of $\mathscr{C}$, Θ and $Q_\theta(c)$. For example, we may take diffusion processes of matter instead of heat transfer (this example will be treated in a subsequent paper). We may also find examples in biology or economics.

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