SHORTER COMMUNICATIONS

THERMOKINETIC ANALYSIS OF HEAT CONDUCTION

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(Received 2 January 1964 and in revised form 17 June 1964)

NOMENCLATURE

		.,
с,	specific heat;	х,
Ε,	internal energy per unit volume;	x_1, x_2, x_3
f,	a positive-valued function definable	X_{ν} ,
	within the volume element, dV ; an	
	integrating factor;	у,
a	a positive function of temperature	23
g,		
- /	only;	German sy
<i>8</i> α',	gradient of g in the a'th direction,	
	$\partial g/\partial x_{\alpha};$	સ. સં
Ι,	a variational integral;	L.
J_{ν} ,	the ν 'th flux of a conservative	
,	variable;	
<i>k</i> ,	k_1, k_2 , or k_3 ; thermal conductivity	Greek sym
	of isotropic body;	a_i or a_j ,
k_{α} ,	thermal conductivity in the a'th	
n_{α} ,	direction;	άi or άi,
k k k ata		<i>~;</i> 01 <i>~j</i> ,
$k_{\alpha 0}, k_{\alpha 1}, k_{\alpha 2},$ etc.	coefficients in the expansion of k_{α}	
	as a power series of $\partial T/\partial x_{\alpha}$, con-	× ×
	stants or functions of position only;	ãi or ãj,
$k_{\alpha\beta},$	thermal conductivity relating the	· •
,	heat flux in the a'th direction caused	ãi or ãj,
	by the temperature gradient in the	
	β 'th direction; constants or func-	
	tions of position only;	
$k_{\alpha\beta\gamma},$	non-linear part of thermal con-	δ,
Γαβγ	ductivity relating the heat flux in	υ,
	the a 'th direction caused by the	9
		д,
	product of the temperature gradi-	
	ents in the β 'th and γ 'th directions;	ε,
	constants or functions of position	ζ,
	only;	
$k_{\alpha x}$,	position dependent part of thermal	ρ,
	conductivity; a positive-valued func-	φ,
	tion;	
<i>k</i> _T ,	temperature dependent part of	
	thermal conductivity;	Subscripts
п,	a constant not equal to -1 and is	$a, \beta, \text{ or } \gamma$
,	independent of direction;	i, j,
S	entropy per unit volume;	
5,		ν,
$S, \\ \tilde{S}, \\ T, \\ T_{\alpha'}, $	entropy of the volume element, dV ;	
Τ,	temperature;	
T_{α}' ,	gradient of T in the a'th direction,	IN 1954, C
	$\partial T/\partial x_{\alpha};$	tinuous sys
1,	time;	ditions and
-	,	

V,	volume;
<i>x</i> ,	$x_1, x_2, \text{ or } x_3;$
$x_1, x_2, x_3, X_3, X_{33}$	co-ordinates; thermodynamic force associated
<i>v</i> ,	with the v'th flux;
у,	steady state distribution function of
	temperature, a function of position.
erman symbols	
જ. જ.	thermokinetic potential;
Ē.	the time rate of change of thermo- kinetic potential, d 2 /dt.
reek symbols	
ai or aj,	a conservative variable per unit volume;
åi or åj,	the time rate of change of a con- servative variable per unit volume; da_i/dt or da_j/dt respectively;
ãi or ãj,	a conservative variable in the volume element, dV ;
ăi or ăj,	the time rate of change of a con- servative variable in the volume element, dV ; $d\bar{\alpha}_i/dt$ or $d\tilde{\alpha}_j/dt$ respectively;
δ,	a change of some quantity within the volume element, dV
ð,	partial differentiation with respect to position;
ε,	an arbitrarily small quantity;
ζ,	arbitrary function of position which vanishes on the surface;
ρ,	density;
φ,	a state function definable within the volume element, dV .
ubscripts	
$\alpha, \beta, \text{ or } \gamma,$	for co-ordinates; 1, 2, or 3;
i, j,	for conservative variables;

INTRODUCTION

for forces and fluxes.

IN 1954, Glansdorff and Prigogine [1] examined continuous systems with time independent boundary conditions and showed the validity of the following inequality

$$\sum J_{\nu} \, \mathrm{d}X_{\nu} \leqslant 0 \tag{1}$$

for several natural dissipative processes including heat conduction within the system. In equation (1), J is the flux of a conservative variable and X is the corresponding force (entropy change per unit flux). The summation consists of all the independent fluxes and forces within the system and at the boundary. More recently they further examined equation (1) to include mechanical processes and found it to be valid also [2].

In examining the classical hypothesis of the separability of individual processes, the present author [3] showed that the left-hand side of equation (1) is integrable for all irreversible processes separable by a linear transformation of the fluxes and forces so that it becomes a total differential:

$$d\mathbf{\hat{z}} = \sum_{\nu} J_{\nu} \, \mathrm{d}X_{\nu} \tag{2}$$

The inequality, equation (1), was shown [3] to be valid for all irreversible processes for a discontinuous system. Thus the function $\mathbf{\hat{x}}$ can only decrease with time and has been given the name of thermokinetic potential. It has since been shown [4] that the inequality is valid for continuous systems in general since it is a result of the second law inequality, provided that each small volume element in the continuous system is thermodynamically stable, in the sense of the second law, when isolated by itself and when all the irreversible processes are frozen. This is most easily shown [4] by expressing the time rate of equation (2) as a volume integral:

$$\dot{\mathbf{g}} = \int_{V} \sum_{i} \sum_{j} \frac{\partial^2 \dot{\mathbf{S}}}{\partial \tilde{a}_i \, \partial \tilde{a}_j} \, \dot{\tilde{a}}_i \, \dot{\tilde{a}}_j < 0 \tag{3}$$

where \hat{S} is the entropy of the small volume element, dV, \hat{a} is a conservative variable in the volume element and $\dot{\hat{a}}$ is the time rate of change of the conservative variable. Let S and a be the corresponding quantities per unit volume; then equation (3) can be represented by:

$$\dot{\mathbf{\mathfrak{T}}} = \int_{V} \mathrm{d}V \sum_{i} \sum_{j} \frac{\partial^{2} S}{\partial a_{i} \partial a_{j}} \dot{a}_{i} \dot{a}_{j} < 0.$$
(3a)

The double summation within the integral consists of all the conservative variables and can only be negative or zero according to the second law of thermodynamics. Since this is true for each volume element, a more general inequality would be

$$\int_{V} f \, \mathrm{d}V \sum_{i} \sum_{j} \frac{\partial^2 S}{\partial a_i \, \partial a_j} \, \dot{a}_i \, \dot{a}_j \leqslant 0 \tag{4}$$

where f is any positive-valued function definable within each volume element. The factor f can be considered as an integrating factor if the left-hand side of equation (4) becomes the time derivative of a state function or the following becomes a total differential:

$$\mathfrak{F} \delta = \int_{V} f \, \mathrm{d}V \sum_{i} \sum_{j} \frac{\partial^{2}S}{\partial a_{i} \partial a_{j}} \dot{a}_{i} \, \delta a_{j}$$
(5)

Since \mathfrak{T} can only decrease with time, it becomes a minimum at the steady state. Equation (5) thus can be used for the variational calculation of all steady-state problems.

Some discussion of the integrability of equation (2) has been given by Prigogine and Balescu [5] and by the present author [4, 6]. The main problem is to find the integrating factor and, for systems where the integrating factor can be shown to be non-existent, to study the stability of such a kinetic system. For the heat conduction problem Glansdorff and Prigogine [2] proposed a successive-approximation procedure in which they first assume a temperature distribution, integrate equation (5) without the integrating factor, minimize the integral to obtain a new temperature distribution and repeat the procedure. But in this manner they presuppose the existence of a stable steady state and the procedure would not converge if such state did not exist. It seems more interesting and certainly more desirable to find exact variational integrals from equation (5) so that the existence of a stable steady state is assured. It is the purpose of this paper to find these integrals for some heat conduction problems in which the integrating factor can be easily obtained and to prescribe a general method for obtaining these integrals. The technique is believed to be new and many integrals, even though obvious from this technique, have not been heretofore presented.

THE THERMOKINETIC POTENTIAL

In the problem of heat conduction, the only conservative variable of interest is the internal energy, E (per unit volume). Consider a volume element $dV = dx_1 dx_2 dx_3$ in the solid body. For such a volume element it is readily seen from thermodynamics that:

$$\left(\frac{\partial S}{\partial E}\right)_{v} = \frac{1}{T} \tag{6}$$

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E}\right)_V = -\frac{1}{c\rho T^2}$$
(7)

and

$$\frac{\partial E}{\partial t} = c \rho \, \frac{\delta T}{\delta t} \tag{8}$$

where c is the specific heat and ρ is the density of the volume element. Now let k_{α} ($\alpha = 1, 2, 3$) be the thermal conductivity in the a'th direction; an energy balance shows that

$$\frac{\partial E}{\partial t} = \left[\sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \left(k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} \right) \right]. \tag{9}$$

Substituting equations (7), (8) and (9) into equation (5) gives

$$\partial \mathbf{\mathfrak{T}} = -\int_{V} \frac{f \, \mathrm{d}V}{T^2} \, \delta T \sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \left(k_{\alpha} \, \frac{\partial T}{\partial x_{\alpha}} \right) \tag{10}$$

Integrating by parts using

$$\frac{f\delta T}{\overline{T}^2} \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{f\delta T}{\overline{T}^2} k \frac{\partial T}{\partial x} \right) - k \frac{\partial T}{\partial x} \frac{\partial}{\partial x} \left(\frac{f\delta T}{\overline{T}^2} \right), (11)$$

and changing one of the volume integrals by a surface integral using Green's theorem, it is seen that for constant surface temperatures ($\delta T = 0$ everywhere on the surface),

$$\delta \mathbf{\hat{z}} = \int_{V} \mathrm{d} V \sum_{\alpha} k_{\alpha} \, \frac{\partial T}{\partial x_{\alpha}} \, \frac{\partial}{\partial x_{\alpha}} \left(\frac{f \delta T}{T^{2}} \right). \tag{12}$$

By finding an integrating factor f, it is possible to make equation (12) a total differential. Then for any temperature distribution in the body, a thermokinetic potential \mathfrak{T} can be defined. Such a potential becomes a minimum at the steady-state temperature distribution and therefore can be used as a variational integral. For example, when $k_{\alpha} = k$ for all α in an isotropic body, let $f = 2T^2/k$ which is always a positive quantity. Equation (12) becomes

$$\delta \mathbf{\hat{z}} = \int_{V} \mathrm{d}V \sum_{\alpha} k \, \frac{\partial T}{\partial x_{\alpha}} \, \delta \, \frac{2}{k} \left(\frac{\partial T}{\partial x_{\alpha}} \right). \tag{13}$$

Equation (13) is a total differential when k is a constant. A thermokinetic potential can be defined as

$$\mathbf{\hat{z}} = \int_{V} \mathrm{d}V \sum_{\alpha} \left(\frac{\partial T}{\partial x_{\alpha}}\right)^{2} \tag{14}$$

which is the usual variational integral used for the case of constant thermal conductivity in an isotropic body.

To show that many variational integrals can be readily obtained from equation (12), consider that $f = gT^2$, with g being a positive function of temperature only. Equation (12) becomes

$$\delta \mathbf{\mathfrak{T}} = \int_{V} \mathrm{d} V \sum_{\alpha} k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} \,\delta\left(g \frac{\partial T}{\partial x_{\alpha}}\right). \tag{15}$$

Equation (15) is obviously a total differential for all the following cases:

(i) k_{α} are constants: Let g = 2,

$$\mathfrak{T} = \int_{\Gamma} \mathrm{d} V \sum_{\alpha} k_{\alpha} \left(\frac{\partial T}{\partial x_{\alpha}}\right)^2 \tag{16}$$

- (ii) k_{α} are functions of position only: Let g = 2 and a thermokinetic potential same as equation (16) is obtained.
- (iii) $k_{\alpha} = k_T(T)$ for all α and k_T is a function of temperature only: Let $g = 2k_T$

$$\mathbf{\mathfrak{T}} = \int_{\Gamma} \mathrm{d} V \sum_{\alpha} \left(k_{\alpha} \, \frac{\partial T}{\partial x_{\alpha}} \right)^{2} \tag{17}$$

(iv) k_{τ} are such that

$$k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} = \sum_{\beta=1}^{3} k_{\alpha\beta} \frac{\partial T}{\partial x_{\beta}}, \qquad \alpha = 1, 2, 3 \qquad (18)$$

where $k_{\alpha\beta}$ are constants or functions of position only and obey the Onsager reciprocity relations:

$$k_{\alpha\beta} = k_{\beta\alpha} \tag{19}$$

Then let g = 2,

$$\mathbf{\mathfrak{T}} = \int_{V} \mathrm{d}V \sum_{\alpha} \sum_{\beta} k_{\alpha\beta} \left(\frac{\partial T}{\partial x_{\alpha}} \right) \left(\frac{\partial T}{\partial x_{\beta}} \right)$$
(20)

(v) $k_{\alpha} = k_{\alpha x}(x_1, x_2, x_3)k_T(T)$ for all α with $k_{\alpha x}$ being a positive function of position only and k_T being that of temperature only: Let $g = 2k_T$

$$= \int_{V} \mathrm{d}V \, k_{T^{2}} \sum_{\alpha} k_{\alpha \alpha} \left(\frac{\partial T}{\partial x_{\alpha}}\right)^{2} \tag{21}$$

(vi) k_{α} is a function of position and of $\partial T/\partial x_{\alpha}$: Let $(\alpha = 1, 2, 3)$

$$k_{\alpha} = k_{\alpha 0} + k_{\alpha 1} \frac{\partial T}{\partial x_{\alpha}} + k_{\alpha 2} \left(\frac{\partial T}{\partial x_{\alpha}} \right)^2 + \ldots \qquad (22)$$

where $k_{\alpha 0}$, $k_{\alpha 1}$, etc., are constants or functions of position only. Then let g = 1,

$$\mathbf{\hat{z}} = \int_{V} \mathrm{d}V \sum_{\alpha} \left[\frac{k_{\alpha 0}}{2} \left(\frac{\partial T}{\partial x_{\alpha}} \right)^2 + \frac{k_{\alpha 1}}{3} \left(\frac{\partial T}{\partial x_{\alpha}} \right)^3 + \dots \right].$$
(23)

(vii) k_{α} are such that ($\alpha = 1, 2, 3$)

$$k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} = \sum_{\beta=1}^{3} k_{\alpha\beta} \frac{\partial T}{\partial x_{\beta}} + \frac{1}{2} \sum_{\beta=1}^{3} \sum_{\gamma=1}^{3} k_{\alpha\beta\gamma} \frac{\partial T}{\partial x_{\beta}} \frac{\partial T}{\partial x_{\gamma}}$$
(24)

where $k_{\alpha\beta}$ and $k_{\alpha\beta\gamma}$ are constants or functions of position only with $k_{\alpha\beta}$ satisfying equation (19) and $k_{\alpha\beta\gamma}$ satisfying the separability condition [3] (totally symmetric):

$$k_{\alpha\beta\gamma} = k_{\beta\alpha\gamma} = k_{\gamma\alpha\beta} = \dots$$
(25)

Then let g = 1,

$$\mathbf{\hat{z}} = \int_{V} d\mathcal{V} \left[\sum_{\alpha} \sum_{\beta} \frac{k_{\alpha\beta}}{2} \left(\frac{\partial T}{\partial x_{\alpha}} \right) \left(\frac{\partial T}{\partial x_{\beta}} \right) + \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \frac{k_{\alpha\beta}}{6} \left(\frac{\partial T}{\partial x_{\alpha}} \right) \left(\frac{\partial T}{\partial x_{\beta}} \right) \left(\frac{\partial T}{\partial x_{\gamma}} \right) \right]$$
(26)

All the foregoing cases are only for g being a constant or a function of temperature only. With other possibilities for g, it is easily realized that a thermokinetic potential and hence a variational integral can be obtained for many problems of heat conduction.

THE INTEGRATING FACTOR

In order to define a thermokinetic potential in the general case of heat conduction, it is necessary to find a positive-valued function f so that equation (12) is a total differential. This certainly will be the case if equation (12) can be expressed as

$$\delta \mathbf{\hat{x}} = \int_{V} \mathrm{d}V \,\delta\phi \tag{27}$$

where ϕ is a state function definable within each volume element in the body. Such a function would vary with the temperature distribution according to equation (12):

$$\delta\phi = \left(\sum_{\alpha} k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} \frac{\partial g}{\partial x_{\alpha}}\right) \delta T + g\left(\sum_{\alpha} k_{\alpha} \frac{\partial T}{\partial x_{\alpha}} \delta \frac{\partial T}{\partial x_{\alpha}}\right)$$
(28)

where $g = f/T^2$. To save some writing, equation (28) is expressed as:

$$\delta \phi = (\sum_{\alpha} k_{\alpha} T_{\alpha}' g_{\alpha}') \, \delta T + g \sum_{\alpha} k_{\alpha} T_{\alpha}' \, \delta T_{\alpha}'.$$
(29)

Equation (29) indicates that ϕ can be considered as a function of T, T_1' , T_2' , and T_3' within each volume element and, if $\delta \phi$ is a total differential, the following should be valid:

$$\frac{\partial (\Sigma k_{\alpha} T_{\alpha}' g_{\alpha}')}{\partial T_{\beta}'} = T_{\beta}' \frac{\partial (gk_{\beta})}{\partial T} \qquad \beta = 1, 2, 3 \quad (30)$$

and

$$T_{\alpha}' \frac{\partial (gk_{\alpha})}{\partial T_{\beta}'} = T_{\beta}' \frac{\partial (gk_{\beta})}{\partial T_{\alpha}'} \qquad \alpha \neq \beta = 1, 2, 3 \quad (31)$$

Equations (30) and (31) are a set of six partial differential equations from which the function g could be found. It is not necessary to solve these equations completely. Any positive-valued function g which satisfies both equations (30) and (31) will make equation (12) a total differential. In solving these equations, g and the k_{α} 's are considered s functions of T, T_1', T_2' , and T_3' in each volume element. If it is impossible to define a thermo-kinetic potential for the system, then according to previous arguments [4] the system may not be stable and a stationary steady state may not exist.

As an example of finding the function g from equations (30) and (31), consider that g is a function of temperature only. Then equation (30) can be solved to give

$$\ln g = \int \frac{T_{\beta}'(\partial k_{\beta}/\partial T) dT}{k_{\beta} T_{\beta}' + \sum_{\alpha} (T_{\alpha}')^{\alpha} (\partial k_{\alpha}/\partial T_{\beta}')}$$
$$\beta = 1, 2, 3 \qquad (32)$$

and equation (31) becomes

$$T_{\alpha}'\frac{\partial k_{\alpha}}{\partial T_{\beta}'} = T_{\beta}'\frac{\partial k_{\beta}}{\partial T_{\alpha}'} \qquad \alpha \neq \beta = 1, 2, 3$$
(33)

which is the Onsager reciprocity relation, equation (19), for the linear case, equation (18), and implies the separability condition, equation (25), for the non-linear case, equation (24). Now it is readily seen from equation (32) that g can be taken as a constant if k_{α} are constants, case (i), or if they are functions of position only, case (ii), or if they are functions of both temperature gradient and position, cases (iv), (vi) and (vii). For case (iii), $k_{\alpha} = k_T(T)$ for all α , substituting into equation (32) gives $g = \text{const } k_T$. For case (v), $k_{\alpha} = k_{\alpha x} k_T$ for all α , substituting into equation (32) gives $g = \text{const } k_T$ also. This covers all the seven cases discussed previously. Now by using equation (32) the function g can be obtained also for the following cases:

(viii) k_{α} can be expressed as $(T_{\alpha}')^n k_{\alpha x}(x_1, x_2, x_3) k_T(T)$ where *n* is a constant independent of α and is not equal to -1: Substituting into equation (32) gives

$$g = \operatorname{const} (k_T)^{1/n+1} \tag{34}$$

which gives the following thermokinetic potential from equation (15)

$$\mathfrak{T} = \int_{V} \mathrm{d}V(k_T)^{1/n+1} \sum_{\alpha} k_{\alpha}(T_{\alpha}')^2.$$
(35)

The constant in equation (34) has been taken as n + 2.

(ix) $k_{\alpha} = k_{\alpha x}(x_1, x_2, x_3)k_T(T) + k_{\alpha 0}/T_{\alpha}'$ where $k_{\alpha 0}$ are constants or functions of position only. Substituting into equation (32) gives g equal to k_T . The following variational integral is obtained:

$$\mathbf{\mathfrak{T}} = \int_{V} \mathrm{d}V \, k_T \sum_{\alpha} T_{\alpha}' \left(k_{\alpha 0} + \frac{k_{\alpha a} k_T T_{\alpha}'}{2} \right) \qquad (36)$$

It is probably not necessary to work out more examples. Those who have specific problems can start from equations (30) and (31), find a function g, or f/T^2 , and substitute into equation (12).

THE STEADY STATE

Although the steady-state temperature distribution corresponds to the minimum of the thermokinetic potential which depends on the function g, the minimization condition is fortunately independent of g.

Let $T(x_1, x_2, x_3) = y(x_1, x_2, x_3)$ be the steady-state distribution, then $\delta \mathfrak{T} = 0$ for all small weak variations around such a distribution. Describe the variation by

$$T(x_1, x_2, x_3) = y(x_1, x_2, x_3) + \epsilon \zeta(x_1, x_2, x_3) \quad (37)$$

with ϵ being an arbitrarily small quantity and ζ an arbitrary function which vanishes on the surface. Substituting into equation (10) gives the following minimization condition

$$\delta \mathbf{\hat{z}} = -\epsilon \int_{V} g\zeta \, \mathrm{d}V \sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \left(k_{\alpha} \frac{\partial y}{\partial x_{\alpha}} \right) = \mathbf{0}$$
(38)

Equation (38) can be obtained also from equation (12) by substituting equation (37). Now since both g and ζ are definable within each volume element and since ζ is an arbitrary function, equation (38) can be satisfied if and only if y satisfies the following partial differential equation

$$-\sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \left(k_{\alpha} \frac{\partial y}{\partial x_{\alpha}} \right) = 0$$
 (39)

which is simply the steady-state condition for all heat conduction problems.

This property of the thermokinetic potential enables us to find g from any variational integral. Let the variational integral be

$$I = \int_{V} \phi(x_1, x_2, x_3, T_1', T_2', T_3') \,\mathrm{d}V \tag{40}$$

For the same variation as equation (37), the change of the integral is

$$\delta I = \epsilon \int_{V} \zeta \left(\frac{\partial \phi}{\partial T} - \sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \frac{\partial \phi}{\partial T_{\alpha}'} \right) \mathrm{d}V \qquad (41)$$

Since ζ is an arbitrary function, the minimization condition of I is

$$\frac{\partial \phi}{\partial T} - \sum_{\alpha} \frac{\partial}{\partial x_{\alpha}} \frac{\partial \phi}{\partial T_{\alpha}} = 0$$
 (42)

which should be equivalent to equation (39). It is possible to factor out the left-hand side of equation (39) from the left-hand side of equation (42). The residual factor is the function g as is obvious from a comparison between equations (38) and (41). This procedure can be verified by calculating g from all the variational integrals obtained previously. It indicates also that if a function g cannot be found from equations (30) and (31) there probably exists no variational integral. Then caution should be given to the possible instability of the steady-state.

Without using a variational integral, it is also possible to find the steady-state temperature distribution from equation (10) or equation (12). Numerically it is only necessary to introduce a number of parameters into the function v and to demand equation (38) or equation (39) to be valid for the independent variation of each parameter. Analytically it is of course equivalent to the solution of equation (39). Another way is to simplify the variational integral or to integrate equation (12) by assuming a spatial distribution of certain quantities such as k_{α} . The variational integral, equation (16), is then minimized to obtain a temperature distribution. A new spatial distribution of k_{α} is then introduced and the minimization repeated. Such successive-approximation procedures are similar to the one proposed by Glansdorff and Prigogine [2]. They all have the assumption that a stable steady state exists and therefore may not converge if such a state does not exist. It would be much safer to take the trouble of finding a function g from equations (30) and (31) so as to formulate an exact variational integral.

DISCUSSION AND SUMMARY

It is worth mentioning here that the rate of entropy production, a function which always exists and is definable for all macroscopic kinetic systems, describes also the kinetic behavior of a non-equilibrium state. Unfortunately, as shown by Cahn and Mullins [7], a steady state in the simplest heat conduction problem does not correspond to the state of minimum rate of entropy production. Starting with a uniform slab at temperature T_1 and at time zero maintaining the temperature at one face at $T_2 (> T_1)$ and that at the other face at T_1 , one can easily show [6] that as time elapses the rate of entropy production first decreases, passes through a minimum, and then increases and approaches a steady-state value. Such behavior will never happen to the thermokinetic potential which can only decrease with time as shown by equation (4). The condition of minimum thermokinetic potential corresponds exactly to that of the steady-state as shown by equation (39) which is independent of the integrating factor f, or gT^2 . The thermokinetic potential thus always can serve as a variational integral.

The thermokinetic potential is in general definable from equation (5) after finding an integrating factor, f, such that equation (5) is a total differential. For heat conduction problems with constant surface temperatures, the thermokinetic potential is definable from equation (12) in which the function f/T^2 , or g, has to satisfy equations (30) and (31). The function g and hence the thermokinetic potential can be easily obtained for many problems as illustrated. These include isotropic solids whose thermal conductivity can be expressed as a function of temperature only, or of position only, or as a product of the two functions, and anisotropic solids whose thermal conductivity is a function of both position and temperature gradients. If the function g cannot be found from equations (30) and (31), it is indicated that a variational integral may not exist by showing that the function g can be obtained from the variational integral if it existed. This is achieved simply by comparing equation (42) with equation (39). Thus it is implied that a variational integral can be obtained from the thermokinetic potential and vice versa.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. R. A. Oriani of this Laboratory, for bringing to his attention the recent work of Glansdorff and Prigogine and for reading the manuscript. He wishes also to thank Dr. Y. T. Chou, also of this Laboratory, for some discussions.

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