

THE VARIATIONAL PRINCIPLE REPLACING THE PRINCIPLE OF MINIMUM ENTROPY PRODUCTION FOR COUPLED NON-STATIONARY HEAT AND MASS TRANSFER PROCESSES WITH CONVECTIVE MOTION AND RELAXATION

STANISLAW SIENIUTYCZ

Institute of Chemical Engineering at the Warsaw Technical University, 00-645 Warsaw,
 Warynskiego 1, Poland

(Received 23 February 1977 and in revised form 25 January 1980)

Abstract—It is a well known fact [1] that the variational theorem of minimum entropy production does not apply for non-stationary processes and/or in the presence of convection. For such processes a new thermodynamic functional of the Hamiltonian type replacing the functional of entropy production is given in this work. The stationarity conditions of this functional are the hyperbolic equations of coupled energy and mass transport which take into account the effects of non-stationarity and macroscopic motion in mechanical equilibrium. The engineering significance of the variational principle given consists in finding approximate fields of temperature and concentrations with the help of direct variational methods.

NOMENCLATURE

a_0^i, \dots, a_{n-1}^i , coefficients of equations (40), (41) and (43) found for i th solution of equation (33) when $D = D_i$;

C, thermostatic matrix of capacities, equations (19), (20) and (26);

c_0 , constant velocity of wave propagation;

C_p , $\left(\frac{\partial h}{\partial T}\right)_p$, heat capacity;

c_q , $\left(\frac{\partial h}{\partial T^{-1}}\right)_p$, thermostatic coefficient for pure heat transfer; $c_q = C_p T^2$;

c_{im} , thermostatic coefficients called capacities, defined by (19) and (20);

col $(m_0, m_1, \dots, m_{n-1})$, column vector of coefficients m_0, m_1, \dots, m_{n-1} ;

D_q , thermal diffusivity of pure heat transfer process;

D_0, D_1, \dots, D_{n-1} , Eigendiffusivities, the roots of characteristic equation;

\tilde{D} , =diag $(D_0, D_1, \dots, D_{n-1})$, diagonal matrix of Eigendiffusivities;

d , diameter of solid particle;

E, diag $(1, 1, \dots, 1)$ unitary matrix;

F autonomous part of Lagrangian, equations (8) and (9);

g , gravity acceleration;

h , enthalpy per mass unit of mixture;

I, \tilde{I} , total entropy production functional and its four-dimensional counterpart, equations (4) and (6), respectively;

J_q, heat flux vector;

k_t, k_x, \dots, k_z , undetermined coefficients of equation (12);

k_q , thermal conductivity, $k_q = L_q T^2$;

L_q , Onsager's coefficient for pure heat transfer;

L, = $[L_{ik}]$, matrix of Onsager's coefficients;

M, = $[m^0, m^1, \dots, m^{n-1}]$, principal matrix of Eigenvalue problem;

m^i , = col $(m_0^i, \dots, m_{n-1}^i)$, column vector of the i th solution of equation (33) for $D = D_i$;

m_s , mass of solid sphere;

P, normal transfer potential, equations (30) and (31);

P, = col $(P^0, P^1, \dots, P^{n-1})$, column vector of the normal transfer potentials found for the Eigendiffusivities D_0, D_1, \dots, D_{n-1} , respectively;

Q, col $[T^{-1} - T_0^{-1}, \dots, (\mu_{n-1}/T) - (\mu_{n-10}/T_0)]$, column vector of the original transfer potential increments;

r, radius vector with the co-ordinates x, y and z ;

S, action functional;

s , entropy of mass unit of mixture;

T , absolute temperature;

T_0 , constant reference temperature, e.g. temperature at infinity;

t , time;

V , volume;

v, v_x, v_y, v_z , constant vector of barycentric velocity;

x_s , Cartesian co-ordinate (x, y or z);

y , mass fraction;

z , vertical co-ordinate.

Greek symbols

Δ , increment: e.g. $\Delta T^{-1} = T^{-1} - T_0^{-1}$ etc.

δ , variation;

ρ , density of mixture;

μ_k ,	chemical potential of the component k ;
$\tilde{\mu}_k$,	$\mu_n - \mu_k$;
$\bar{\mu}$,	dynamic viscosity of fluid;
τ_q ,	relaxation time in pure heat transfer process;
Ω ,	four-dimensional volume, $d\Omega = dx dy dz dt$;
ϕ ,	non-autonomous part of Lagrangian;
∇^2 ,	Laplace operator.

Superscripts

T,	transpose matrix;
-1,	reverse matrix.

Subscripts

i, k ,	components i and k ;
n ,	last component;
0,	reference state;
q ,	heat;
s ,	number of Cartesian co-ordinate.

1. INTRODUCTION

IRRESPECTIVE of the vast number of the searches for variational principles of the classical type (see e.g. the review by Finlayson and Scriven [2]) suitable classical functionals have so far not been obtained, which would lead to the partial differential equations describing the coupled processes of non-stationary energy and mass transport in the presence of macroscopic motion. Some investigators, e.g. Yourgrau and Mandelstam [3], claim that such functionals probably do not exist and that only the equations of thermodynamically reversible phenomena can be derived from the stationarity principles of the exact functionals. The recognized method of the local potential due to Glansdorff and Prigogine [4] does not introduce the functional in the classical meaning e.g. such as that of Hamilton's type. The advantages and shortcomings of this approach as well as of other 'restricted' variational methods are not analysed in this study; see, however, Finlayson and Scriven [2].

Vujanovic, in his series, see e.g. [5, 6], was able to show that some variational formulation exists, at least for the hyperbolic equations of change describing heat conduction and fluid flow, this formulation being possible due to the presence of a non-autonomous term, $\exp(t/\tau_q)$ in the action functionals. The role of such terms was systematically analysed by the present author in [7, 8] where the various forms of the hyperbolic equations of change were also considered, depending on the time-space transformations applied, in the systems with moving media. Furthermore, Lebon [9] has proved that an interesting formulation can also be obtained (for the pure heat transfer case, linear or non-linear) which leads to the set of conservation and phenomenological equations. In connection with the above findings it should be clearly pointed out that, as shown by Finlayson [10], the crucial test for deriving a variational principle associated to a set of differential equations is the existence of a symmetric Fréchet derivative. Clearly the class of equations considered by Vujanovic and

Lebon, as well as those in the present work belong to this category.

Also the existence of Prigogine's principle of minimum entropy production [1]* involving a classically defined functional, appears to contradict the opinion of the non-existence of variational principles of classical type for irreversible processes, if the assumption of the constancy of phenomenological coefficients incorporated in this principle is accepted. This principle, however, is valid only for time-dependent processes, i.e. when relaxation effects are not involved and the macroscopic motion is excluded. Despite a number of the restrictions the principle is of considerable theoretical significance as a general variational principle of classical type which accounts for mutual coupling of irreversible phenomena. Also of importance are practical aspects of the principle as it is helpful in the formulation of a suitable expression for the local potentials [4] which are used to find the solutions of the transport equations in the case of variable phenomenological coefficients. In this connection attempts to find a classical type variational principle which would, to some extent at least, generalize this (Prigogine's) principle, are still attractive.

This study will be concerned with non-stationary irreversible processes of coupled† energy and mass transfer with convection occurring under mechanical equilibrium conditions. The pure heat transfer case will be analysed first and experience gained from it will be used to investigate the simultaneous energy and mass transfer. A variational principle will be formulated which may be regarded as an analogue of the principle of minimum entropy production for non-stationary processes with macroscopic motion. Although the principle itself will not be related to the minimum of entropy production, however, as we shall show, it will resolve itself to Prigogine's principle when the macroscopic motion and relaxation effects are disregarded. The fact that these two effects will be taken into account will permit the new principle to describe a larger number of fundamental phenomena than the principle of minimum entropy production usually does. This fact is especially important for the heat and mass transfer specialists when investigating the solutions of the heat and mass transfer equations in the case of the difficult, highly non-stationary, processes. Using the principle advanced here such solutions can be effectively obtained with the help of direct variational methods (see [11, 12] and Section 6). The concept of so-called normal transfer potentials, Section 4, should be useful for engineers investigating the solutions of heat and mass transfer equations of many technical processes. These facts will to some extent compensate for the shortcomings of the method which result from the fact, that the Prigogine

* For a special case of this principle, see equation (4) in this paper.

† The uncoupled processes have been analysed in [7] which may be treated as the first part of this work.

assumption of constancy of phenomenological coefficients will affect, in the present case, not only Onsager's coefficients, but also the thermostatic coefficients called capacities, see equations (3), (19), (20) and (25) in this paper. The capacities appear in the non-dissipative terms of the process equations which are not present in Prigogine's principle since it deals with the purely dissipative cases [4, 11]. Investigations into a possible formulation of variational theorems which would abandon the assumption mentioned should be subject of a further effort.

2. CONSTRUCTION OF VARIATIONAL PRINCIPLE FOR PURE HEAT TRANSFER

To introduce the reader to the formulation of variational principle for non-stationary processes with macroscopic motion the pure heat transfer in a moving solid is analysed first. A counterpart of the principle of minimum entropy production is then relatively easy to obtain and the origin of functionals presented in this work can be explained clearly. This case serves as an excellent introduction for the much more difficult case of coupled processes, Sections 3–5.

The hyperbolic equation describing pure heat transfer in a moving rigid solid is obtained directly from the Maxwell phenomenological equation [9] (containing relaxation term for heat flux) and the energy conservation law. For the Galillean frames the result is*

$$\rho \frac{dh}{dt} = -\text{div}(L_q \text{grad } T^{-1}) - \rho \tau_q \frac{d^2 h}{dt^2} \quad (1)$$

where the operators d/dt and d^2/dt^2 are the first and the second substantial derivatives defined respectively as

$$\frac{dT^{-1}}{dt} = \frac{\partial T^{-1}}{\partial t} + \mathbf{v} \text{grad } T^{-1}; \quad (2a)$$

$$\begin{aligned} \frac{d^2 T^{-1}}{dt^2} &= \frac{d}{dt} \left(\frac{dT^{-1}}{dt} \right) = \frac{\partial^2 T^{-1}}{\partial t^2} \\ &+ 2\mathbf{v} \text{grad} \frac{\partial T^{-1}}{\partial t} + \mathbf{v} \text{grad}(\mathbf{v} \text{grad} T^{-1}). \end{aligned} \quad (2b)$$

These definitions should be always remembered when reading this text. The last term on the RHS of equation (1) contains the relaxation time $\tau_q = D_q/c_0^2$ so it describes thermal relaxation effects. This time as well as the wave propagation velocity, c_0 , are assumed as constants.

To investigate the variational principle for equation (1) one must express enthalpy as a function of definite transfer potential e.g. reciprocity of temperature. Also

the relaxation term should utilize with this variable. For this purpose we transform equation (1) to the form containing T^{-1} as the only thermodynamic variable and we take the thermostatic coefficient $c_q = (dh/dT^{-1})_0$ as a constant. The Onsager coefficient L_q is subjected to the same assumption (Prigogine's assumption). With the above assumptions we obtain from equation (1) the linear equation

$$\rho c_q \frac{dT^{-1}}{dt} + L_q \left(\nabla^2 T^{-1} - \frac{d^2 T^{-1}}{c_0^2 dt^2} \right) = 0. \quad (3)$$

We shall show that the variational principle of the classical type exists for equation (3) replacing the variational principle of minimum entropy production, and reducing to the latter in the time-independent case and when the system is at rest.

We will start our reasoning from this latter case for which Prigogine's principle holds. We assume constant temperature at the boundary of the system. Then minimization of the entropy production functional

$$I = \iiint L_q (\text{grad } T^{-1})^2 dx dy dz \quad (4)$$

gives, when $L_q = \text{constant}$, the Euler equation

$$L_q \nabla^2 (T^{-1}) = 0 \quad (5)$$

which is, under the same assumption, the equation for stationary heat transfer.

In order to find the generalized form of functional (4) one may note that using some four-dimensional extension of Lagrangian appearing in equation (4) i.e. considering the functional

$$\begin{aligned} \tilde{I} = \iiint \iiint L_q \left[(\text{grad } T^{-1})^2 \right. \\ \left. - \frac{1}{c_0^2} \left(\frac{dT^{-1}}{dt} \right)^2 \right] dx dy dz dt \end{aligned} \quad (6)$$

the Euler equation takes the form

$$L_q \left(\nabla^2 T^{-1} - \frac{1}{c_0^2} \frac{d^2 T^{-1}}{dt^2} \right) = 0 \quad (7)$$

which is the last term of equation (3). Note that the substantial derivative definitions, equations (2), were used when passing from equation (6) to equation (7). However, equation (7) is still not yet the desired result because it does not describe such non-dissipative phenomena as equations (1) and (3). To take these phenomena into account we assume—and this is a crucial assumption for the mathematical technique used here—that Lagrangian leading to equation (3) can be obtained from Lagrangian of equation (6) after multiplying the last one by some temporary undetermined function $\phi(x, y, z, t)$ which may depend exclusively on the spatial co-ordinates and time. It means that we will consider a non-autonomous functional of the general structure

* The equation (1) is the result of combining: $L_q \text{grad } T^{-1} = \mathbf{J}_q + \tau_q d\mathbf{J}_q/dt$ with $\rho dh/dt = -\text{div} \mathbf{J}_q$ which are respectively the Galillean form of Maxwell equation and energy conservation equation for moving solid.

$$S = \iiint \int F \left(\frac{dT^{-1}}{dt}, \frac{\partial T^{-1}}{\partial x}, \frac{\partial T^{-1}}{\partial y}, \frac{\partial T^{-1}}{\partial z}, T^{-1} \right) \times \phi(x, y, z, t) d\Omega \quad (8)$$

where $d\Omega = dx dy dz dt$ and in our case

$$F = L_q \left[(\text{grad } T^{-1})^2 - \frac{1}{c_0^2} \left(\frac{dT^{-1}}{dt} \right)^2 \right] \quad (9)$$

Our purpose will be to determine function ϕ such that equation (3) will be the Euler equation for the functional defined by equations (8) and (9). Since equation (3) is from its physical nature autonomous (it does not contain the independent variables explicitly) we must examine which conditions must be met so that the Euler equation will not explicitly contain the variables x, y, z and t . Using again the substantial derivative definitions, equations (2) it can be verified that the general form of Euler equation for functional (8) can be written as

$$\frac{d}{dt} \left[\frac{\partial(F\phi)}{\partial \left(\frac{dT^{-1}}{dt} \right)} \right] + \sum_{s=1}^{s=3} \frac{\partial}{\partial x_s} \left[\frac{\partial(F\phi)}{\partial \left(\frac{\partial T^{-1}}{\partial x_s} \right)} \right] = \frac{\partial(F\phi)}{\partial T^{-1}} \quad (10)$$

or after using the differentiation formula for the product $F\phi$ and then dividing both sides by ϕ

$$\begin{aligned} & \frac{d}{dt} \left[\frac{\partial F}{\partial \left(\frac{dT^{-1}}{dt} \right)} \right] + \sum_{s=1}^{s=3} \frac{\partial}{\partial x_s} \left[\frac{\partial F}{\partial \left(\frac{\partial T^{-1}}{\partial x_s} \right)} \right] + \frac{d \ln \phi}{dt} \\ & \times \frac{\partial F}{\partial \left(\frac{dT^{-1}}{dt} \right)} + \sum_{s=1}^{s=3} \frac{\partial \ln \phi}{\partial x_s} \frac{\partial F}{\partial \left(\frac{\partial T^{-1}}{\partial x_s} \right)} = \frac{\partial F}{\partial T^{-1}} \quad (11) \end{aligned}$$

Equation (11) will not explicitly contain independent variables x, y, z and t if the function $\ln[\phi(x, y, z \text{ and } t)]$ will be linear, that is when

$$\phi = \exp(k_t t + k_x x + k_y y + k_z z) \quad (12)$$

where k_t, k_x, k_y and k_z are constants which will be determined after consideration of equations (3), (9), (11) and (12).

Using equations (9) and (12) into equation (11) one obtains

$$\begin{aligned} & L_q \left[\nabla^2 T^{-1} - \frac{dT^{-1}}{c_0^2 dt^2} \right] - k_t L_q \frac{dT^{-1}}{c_0^2 dt} + \\ & k_x L_q \frac{\partial T^{-1}}{\partial x} + k_y L_q \frac{\partial T^{-1}}{\partial y} + k_z L_q \frac{\partial T^{-1}}{\partial z} = 0. \quad (13) \end{aligned}$$

Hence, after comparing equations (3) and (13) one finds

$$k_t = -\frac{\rho c_0^2 c_q}{L_q}, \quad k_x = k_y = k_z = 0 \quad (14)$$

and after substituting these relations into equation (12)

one finds*

$$\phi = \exp(-\rho c_q c_0^2 t L_q^{-1}) = \exp(c_0^2 t D_q^{-1}). \quad (15)$$

Thus after using equations (8), (9) and (15) one obtains the functional

$$\begin{aligned} S = & \iiint \int \int L_q \left[(\text{grad } T^{-1})^2 - \frac{1}{c_0^2} \left(\frac{dT^{-1}}{dt} \right)^2 \right] \\ & \times \exp(-\rho c_q c_0^2 t L_q^{-1}) d\Omega \quad (16) \end{aligned}$$

replacing the functional entropy production, see equation (4), for the process of pure heat transfer in the presence of macroscopic motion and relaxation effects. It may be easy to verify that the Euler equation for this functional becomes the hyperbolic equation (3) upon simplification of the exponential terms. One can additionally note that if the terms containing time explicitly are disregarded and the solid is at rest ($v = 0$) then the functional S simplifies to the functional (4) of entropy production and equation (3) reduces to the stationary form equation (5). Thus we have obtained the correct variational principle, under the same sort of assumptions as in Prigogine's theorem [1,4].

It is necessary to remember that as pointed out in equation (15) the term $\rho c_q L_q^{-1}$ in the exponential term of equation (15) is precisely equal to the negative reciprocal of heat diffusivity D_q defined in usual manner. It will be of some importance to extend equation (15) to the case of coupled heat and mass transfer processes.

3. EQUATIONS DESCRIBING SIMULTANEOUS HEAT AND MASS TRANSFER

Let us consider an isotropic mixture of n components $k(k = 1, 2, \dots, n)$ under mechanical equilibrium conditions, in which coupled heat and mass transfer occurs. To make the formulae obtained shorter, let us consider the case of no external forces which is equivalent to isobaric condition of the process. The generalization that accounts for the external forces deriving from potential is self-evident. However for more complicated situations e.g. in case of Lorentz forces the generalization of the variational principle presented here is far from being a trivial matter. The constant velocity of motion of the system, v , is defined in the usual manner as the barycentric velocity [1]. Additionally, the assumption mentioned in Section 1 will be made: namely: the phenomenological coefficients that are elements of Onsager's matrix as well as thermostatic coefficients called capacities, being defined below, are taken as constants.

The definition and properties of the capacities result from the formula for the differential of the specific entropy of the system:

* It is only for Galilleian frames that $k_x = k_y = k_z = 0$ and that the function ϕ is the same in moving and stationary media e.g. in Lorentz (relativistic) frames $k_x \neq k_y \neq k_z \neq 0$, i.e. k_i will not vanish, and the scalar product $\mathbf{v} \cdot \mathbf{r}$ will appear in ϕ . However we will not consider this problem in detail, see [8].

$$ds = T^{-1} dh - \sum_{k=1}^{n-1} [(\mu_k - \mu_n) T^{-1}] dy_k \quad (17)$$

and from the formula for a Legendre transformation of function s determined by equation (17), i.e. from the relation

$$d(\mu_n/T) = h dT^{-1} + \sum_{k=1}^{n-1} y_k d[(\mu_n - \mu_k) T^{-1}]. \quad (18)$$

The capacities are defined as partial derivatives of enthalpy h and concentrations y_k with respect to the variables T^{-1} and $[(\mu_n - \mu_k) T^{-1}]$, respectively. In terms of the capacities the differentials dh and dy_i are described as follows:

$$dh = c_{qq} dT^{-1} - \sum_1^{n-1} c_{qk} d[(\mu_k - \mu_n) T^{-1}] \quad (19)$$

$$dy_i = c_{iq} dT^{-1} - \sum_1^{n-1} c_{ik} d[(\mu_k - \mu_n) T^{-1}]. \quad (20)$$

It follows from equation (18) that the capacities result as the second partial derivatives of the function μ_n/T with respect to the variables T^{-1} and $(\mu_n - \mu_k)/T$, that is, they obey the symmetry conditions $c_{kq} = c_{qk}$ and $c_{ik} = c_{ki}$.

Our task will be to find the variational principle leading to the following system of hyperbolic equations [8] describing, in Galilean frames, the coupled heat and mass transfer with macroscopic motion and relaxation:

$$0 = \rho \frac{dh}{dt} + L_{qq} \left(\nabla^2 T^{-1} - \frac{d^2 T^{-1}}{c_0^2 dt^2} \right) - \sum_{k=1}^{n-1} L_{qk} \left\{ \nabla^2 [(\mu_k - \mu_n) T^{-1}] - \frac{d^2 [(\mu_k - \mu_n) T^{-1}]}{c_0^2 dt^2} \right\} \quad (21)$$

$$0 = \rho \frac{dy_i}{dt} + L_{iq} \left(\nabla^2 T^{-1} - \frac{d^2 T^{-1}}{c_0^2 dt^2} \right) - \sum_{k=1}^{n-1} L_{ik} \left\{ \nabla^2 [(\mu_k - \mu_n) T^{-1}] - \frac{d^2 [(\mu_k - \mu_n) T^{-1}]}{c_0^2 dt^2} \right\}. \quad (22)$$

For the system at rest these equations contain d'Alemberts operators replacing the commonly used Laplace operators because relaxation phenomena are not neglected in our description. In equations (21) and (22) as well as in further analysis it is assumed that the velocity of wave propagation, c_0 , is a constant independent of time and location in the system.

For the purpose of operating with a definite set of mutually independent variables the enthalpy and concentration differentials should be expressed in terms of differentials of the transfer potentials, T^{-1} , $[(\mu_1 - \mu_n) T^{-1}]$, ... etc. Using equations (19) and (20) in equations (21) and (22) one can obtain:

$$\rho \left\{ c_{qq} \frac{dT^{-1}}{dt} - \sum_{k=1}^{n-1} c_{qk} \frac{d}{dt} [(\mu_k - \mu_n) T^{-1}] \right\} + L_{qq} \nabla^2 T^{-1} - \sum_{k=1}^{n-1} L_{qk} \nabla^2 [(\mu_k - \mu_n) T^{-1}] - \frac{L_{qq}}{c_0^2} \frac{d^2 T^{-1}}{dt^2} + \sum_{k=1}^{n-1} \frac{L_{qk}}{c_0^2} \frac{d^2 [(\mu_k - \mu_n) T^{-1}]}{dt^2} = 0 \quad (23)$$

$$\rho \left\{ c_{iq} \frac{dT^{-1}}{dt} - \sum_{k=1}^{n-1} c_{ik} \frac{d}{dt} [(\mu_k - \mu_n) T^{-1}] \right\} + L_{iq} \nabla^2 T^{-1} - \sum_{k=1}^{n-1} L_{ik} \nabla^2 [(\mu_k - \mu_n) T^{-1}] - \frac{L_{iq}}{c_0^2} \frac{d^2 T^{-1}}{dt^2} + \frac{L_{ik}}{c_0^2} \frac{d^2 [(\mu_k - \mu_n) T^{-1}]}{dt^2} = 0. \quad (24)$$

The two symmetric matrices are associated with equations (23) and (24), namely the positive defined matrix of Onsager

$$L = \begin{bmatrix} L_{qq} & L_{q1} & \dots & L_{q,n-1} \\ L_{1q} & L_{11} & \dots & L_{1,n-1} \\ \dots & \dots & \dots & \dots \\ L_{n-1,q} & L_{n-1,1} & \dots & L_{n-1,n-1} \end{bmatrix} \quad (25)$$

and the 'thermodynamic' matrix of capacities

$$C = \begin{bmatrix} c_{qq} & c_{q1} & \dots & c_{q,n-1} \\ c_{1q} & c_{11} & \dots & c_{1,n-1} \\ \dots & \dots & \dots & \dots \\ c_{n-1,q} & c_{n-1,1} & \dots & c_{n-1,n-1} \end{bmatrix}. \quad (26)$$

One may note that the elements of matrix C are precisely those which appear in fluctuation theory for quadratic approximation of the entropy excess ΔS_{total} of a large closed non-equilibrium system having a uniform temperature T_0 and chemical potentials μ_{k0} nearly everywhere except for the unit mass part where the temperature is T and chemical potentials are μ_k . Indeed, one has in our isobaric case

$$\Delta S_{\text{total}} = \Delta S - \frac{\Delta h}{T_0} + \sum_{k=1}^{n-1} (\mu_{k0} - \mu_{n0}) T_0^{-1} \Delta y_k \cong \frac{1}{2} \left\{ \Delta T^{-1} \Delta h - \sum_{k=1}^{n-1} \Delta [(\mu_k - \mu_n) T^{-1}] \Delta y_k \right\} \quad (27)$$

after Taylor expansion of Δs with accuracy to the second order terms. Equivalently

$$\Delta S_{\text{total}} = \frac{1}{2} \left\{ c_{qq} (\Delta T^{-1})^2 - 2 \sum_{k=1}^{n-1} c_{qk} \Delta T^{-1} \Delta [(\mu_k - \mu_n) T^{-1}] + \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} c_{ik} \Delta [(\mu_k - \mu_n) T^{-1}] \times \Delta [(\mu_i - \mu_n) T^{-1}] \right\}. \quad (28)$$

This expression is a consequence of the local equilibrium hypothesis of isobaric macroscopic system, see [1,4]. For a stable system C is a negative definite matrix at least in close to equilibrium situations. However the nature of the transfer equations which involve relaxation terms indicates that the system can be far from equilibrium and, then, it can be questioned if C is always negative. Although C (or its reverse) was taken in [4] to be always negative it should be underlined that this negativity condition is not necessary for our purposes. Namely, the construction of the variational principle can be accomplished also when C is not of definite sign. It will be shown that the only requirement is that at least one of the two matrices, L or C , has to be of definite sign.

4. AN EIGENVALUE PROBLEM SIMPLIFYING THE FINDING OF VARIATIONAL PRINCIPLE

We shall show by extension of reasoning presented in Section 2, that the variational principle exists leading to equations (23) and (24). At first glance, however, it seems to be extremely difficult to formulate such a principle because of the complexity of the process equations. Some introductory search is therefore required, this is presented in this section.

The basic concept of the present technique will exploit the notion that the finding of variational formulation will be much more easy if the set of equations (23) and (24) is broken down to the equivalent uncoupled set of equations operating with new transfer potentials for which both symmetric matrices C and L will become simultaneously diagonal. Although it is commonly known that any symmetric quadratic matrix can be broken down to the diagonal form by orthogonal transformations it is not intuitively obvious that the transformation exists which makes two, symmetric matrices both diagonal.

In analytical dynamics theory, cf [13], and especially in the theory of vibrations this fact is, however, well known since it is connected with the transformation of the non-Cartesian form of kinetic energy matrix and potential energy matrix to the two diagonal matrices simultaneously after introducing so called normal (or principal) co-ordinates. It is always possible to accomplish it if at last one of the two matrices considered is of definite sign [13]. It is also known that in such a case the transformation which leads to normal co-ordinates is always a real one [13,14] for the two non-singular symmetric matrices.

Now we will apply the above concept to transform equations (23) and (24) an equivalent form* from which the variational principle will result immediately, on the basis of the variational results of Section 2. Let us suppose that we have multiplied each of relations, equations (23) and (24) by some temporary undetermined multipliers m_0, m_1, \dots, m_{n-1} and then we added the resulting equations together. The equation

obtained is:

$$\begin{aligned}
 0 = & \rho(c_{qq}m_0 + c_{1q}m_1 + \dots c_{kq}m_k + c_{n-1q}m_{n-1}) \frac{dT^{-1}}{dt} \\
 & + \rho(c_{q1}m_0 + c_{11}m_1 + \dots c_{k1}m_k \dots c_{n-1,1}m_{n-1}) \\
 & \times \frac{d[(\mu_n - \mu_1)/T]}{dt} + \rho(c_{qn-1}m_0 + c_{1n-1}m_1 \\
 & + \dots c_{kn-1}m_k \dots + c_{n-1n-1}m_{n-1}) \frac{d[(\mu_n - \mu_{n-1})/T]}{dt} \\
 & + (L_{qq}m_0 + L_{1q}m_1 + \dots L_{kq}m_k \dots L_{n-1, q}m_{n-1}) \\
 & \times \left[\nabla^2 T^{-1} - \frac{d^2 T^{-1}}{c_0^2 dt^2} \right] \\
 & + (L_{q1}m_0 + L_{11}m_1 + \dots L_{k1}m_k + L_{n-1, 1}m_{n-1}) \\
 & \times \left[\nabla^2 \left(\frac{\mu_n - \mu_1}{T} \right) - \frac{d^2 (\mu_n - \mu_1)/T}{c_0^2 dt^2} \right] \\
 & + \dots + (L_{qn-1}m_0 + L_{1n-1}m_1 \\
 & \times \dots L_{kn-1}m_k + L_{n-1n-1}m_{n-1}) \\
 & \times \left[\nabla^2 \left(\frac{\mu_n - \mu_{n-1}}{T} \right) - \frac{d^2 [(\mu_n - \mu_{n-1})/T]}{c_0^2 dt^2} \right] \tag{29}
 \end{aligned}$$

where, for brevity, the substantial derivative operators d/dt and d^2/dt^2 are again introduced. Considering sequentially the coefficients of the terms containing

$$\frac{dT^{-1}}{dt}, \quad \nabla^2 T - \frac{1}{c_0^2} \frac{d^2 T^{-1}}{dt^2},$$

then the terms containing

$$\frac{d[(\mu_n - \mu_1)/T]}{dt}, \quad \nabla^2 \left(\frac{\mu_n - \mu_1}{T} \right) - \frac{d^2 [(\mu_n - \mu_1)T^{-1}]}{c_0^2 dt^2}$$

etc. one can observe that the equation (29) will take the simple 'canonical' form

$$-\rho \frac{dP}{dt} + \rho D \left(\nabla^2 P - \frac{1}{c_0^2} \frac{d^2 P}{dt^2} \right) = 0 \tag{30}$$

where

$$\begin{aligned}
 P \equiv & a_0 \left(\frac{1}{T} - \frac{1}{T_0} \right) + a_1 \left[\left(\frac{\mu_n - \mu_{n-1}}{T} \right) \right. \\
 & \left. - \left(\frac{\mu_n - \mu_{n-1}}{T} \right)_0 \right] \dots \\
 & + \dots a_{n-1} \left[\left(\frac{\mu_n - \mu_{n-1}}{T} \right) - \left(\frac{\mu_n - \mu_{n-1}}{T} \right)_0 \right] \tag{31}
 \end{aligned}$$

and [the symmetry of matrices has been exploited in equations (32) and (33)]

$$\begin{aligned}
 a_0 = & c_{qq}m_0 + c_{q1}m_1 + \dots c_{qk}m_k + \dots c_{qn-1}m_{n-1} \\
 a_1 = & c_{1q}m_0 + c_{11}m_1 \dots c_{1k}m_k + c_{1n-1}m_{n-1} \\
 a_{n-1} = & c_{n-1,q}m_0 + c_{n-1,1}m_1 \dots \\
 & c_{n-1,k}m_k \dots c_{n-1,n-1}m_{n-1} \tag{32}
 \end{aligned}$$

only when a constant D exists, appearing in equations

* This form will be uncoupled with respect to the new dependent variables, i.e. potentials P^i , defined later.

(30) and (33), that the multipliers m_0, m_1, \dots, m_{n-1} , meet the equations

$$\begin{aligned}
 &L_{qq}m_0 + L_{q1}m_1 + \dots + L_{qk}m_k + \dots + L_{qn-1}m_{n-1} \\
 &= -\rho D c_{qq}m_0 + c_{q1}m_1 \dots c_{qk}m_k + c_{qn-1}m_{n-1} \\
 &L_{1q}m_0 + L_{11}m_1 + \dots + L_{1k}m_k + \dots + L_{1n-1}m_{n-1} \\
 &= -\rho D(c_{1q}m_0 + c_{11}m_1 + \dots + c_{1k}m_k + c_{1n-1}m_{n-1}) \\
 &L_{n-1,q}m_0 + L_{n-1,1}m_1 + \dots + L_{n-1,k}m_k \dots \\
 &+ L_{n-1,n-1}m_{n-1} \\
 &= -\rho D(c_{n-1,q}m_0 + c_{n-1,1}m_1 \\
 &+ c_{n-1,k}m_k + c_{n-1,n-1}m_{n-1}). \tag{33}
 \end{aligned}$$

The quantity P obeying equations (30) and (31) is expressed in terms of the excesses of original transfer potentials, with regard to arbitrary reference state, as e.g. constant state at infinity, P will be called normal transfer potential, since, as it will be shown later, n such independent potentials P^i will exist each of which obey the simple separable structure of equation (30). We will not characterize the potential P extensively since they have in our analysis only temporary, significance, and we will return finally to original potentials $1/T, (\mu_n - \mu_1)/T \dots$, etc.

Equations (33) will be consistent only then if the constant D having the dimension of diffusivity, is the root of the characteristic equation:

$$\det(\mathbf{L} + D\rho\mathbf{C}) = 0. \tag{34}$$

This is the so called general Eigenvalue problem for the pencil of matrices \mathbf{L} and $(-\rho\mathbf{C})$ known in algebra [14]. The roots of equation (34) D_0, D_1, \dots, D_{n-1} are Eigenvalues or characteristic roots of the pencil of matrices mentioned. Since matrices \mathbf{L} and $(-\rho\mathbf{C})$ are both symmetric, the characteristic roots, i.e. quantities D_0, D_1, \dots, D_{n-1} , are all real numbers which are all positive when $\mathbf{C} < \mathbf{O}$ and $\mathbf{L} > \mathbf{O}$, see [14, 13].

Because of these properties of the roots, D_0, D_1, \dots, D_{n-1} , and their dimensions of diffusivity we will term them as 'Eigendiffusivities'. The most important physical property of the Eigendiffusivities D_0, \dots, D_{n-1} results from the invariancy of characteristic equation (34). Any non-singular linear transformation of the original transfer potentials, described by the independent equations each of the type of equation (31), transforms the set, equations (23) and (24), into the new set with new coefficients which are the elements of the new matrices \mathbf{L}_1 and \mathbf{C}_1 . For these new matrices the characteristic equation

$$\det(\mathbf{L}_1 + D\rho\mathbf{C}_1) = 0 \tag{35}$$

has the same characteristic roots as equation (34). Thus, the Eigendiffusivities are physical quantities independent of thermodynamic variables used in process description.

For the special case of pure heat transfer equation (34) reduces to

$$L_q + D_q \rho c_q = 0 \tag{36}$$

or since $c_q = -C_p T_0^2$ and $L_q T_0^2 = k_q$, the thermal conductivity, to

$$D_q = \frac{k_q}{\rho C_p} \tag{37}$$

in agreement with the common definition of heat diffusivity.

After solving equation (34) the Eigendiffusivities D_0, D_1, \dots, D_{n-1} become known. For any value of $D_i, i=0, 1, \dots, n-1$, one can now determine numerical values of coefficients $m_0^i, m_1^i, \dots, m_{n-1}^i$ and $a_0^i, a_1^i, \dots, a_{n-1}^i$ from equations (33) and (32), respectively, provided that for each index $i (i=0, 1, \dots, n-1)$ there is defined one additional equation interconnecting $m_0^i, m_1^i, \dots, m_{n-1}^i$ which is called the normalizing condition. The reason for normalization is that equation (33) is homogeneous with respect to m_0, \dots, m_1 and without normalization only ratios between coefficients $m_0^i, \dots, m_1^i, m_{n-1}^i$ would be determined. (Without normalization, the quantities $a_0^i, a_1^i, \dots, a_{n-1}^i$ and P^i would be determined with the accuracy to the constant multipliers only.)

Normalization makes n solutions of equation (33) synonymous for m_0^i, \dots, m_{n-1}^i and consequently defines synonymously n normal potentials P^i each of them obeying equation (30). Note that normalization does not influence the values of Eigendiffusivities D_i .

Although normalization is only a mathematical procedure, and it may be accomplished in many ways, it is useful to normalize coefficients m_0^i, \dots, m_{n-1}^i , in some special manner. Here the normalization is so accomplished that the n column vectors $\mathbf{m}^i = \text{col}(m_0^i, m_1^i, \dots, m_{n-1}^i)$ obey n relations of the form:

$$(\mathbf{m}^i)^T \mathbf{C} \mathbf{m}^i = -1; \quad i = 0, 1, \dots, n-1. \tag{38}$$

Since the vectors \mathbf{m}^i and \mathbf{m}^j for two different Eigenvalues $D_i \neq D_j$ are orthogonal with respect to each of the two matrices $(-\rho\mathbf{C})$ and \mathbf{L} , [14], i.e.

$$(\mathbf{m}^i)^T \mathbf{C} \mathbf{m}^j = (\mathbf{m}^i)^T \mathbf{L} \mathbf{m}^j = 0; \quad i \neq j \tag{39}$$

then, after use of normal transfer potentials and normalization the matrix, \mathbf{C} transforms into a negative unitary matrix, $\text{diag}(-1, -1, -1, \dots, -1)$, and the matrix \mathbf{L} into diagonal matrix, $\text{diag}(\rho D_0, \rho D_1, \rho D_2, \dots, \rho D_{n-1})$. This results from the basic properties of the general Eigenvalue problem [14] as outlined in the Appendix.

Solving the set of equations each the type of equation (33), n times, for $D = D_0, D = D_1, \dots, D = D_{n-1}$ with the use of n normalization conditions,* equation (38), we obtain the definite set of vectors \mathbf{m}^i with the co-ordinates $m_0^i, m_1^i, \dots, m_{n-1}^i$. Then, the coefficients $a_0^i, a_1^i, \dots, a_{n-1}^i$ of the equation (31) are

* An equivalent normalization condition $-\sum_0^{n-1} P_i^2 = \mathbf{Q}^T \mathbf{C} \mathbf{Q}$ might be used where $\mathbf{Q} = \text{col}(\Delta T^{-1}, \Delta(\mu_n - \mu_1) T^{-1} \dots)$. It is indicated by equation (A.6) in the Appendix.

found using equation (32), or equivalently, the matrix formula:

$$a^i = C m^i \tag{40}$$

where $a = \text{col}(a_0, a_1, \dots, a_{n-1})$.

Thus we know the coefficients of equation (31) for $D = D_i$, and we can write n independent definitions for P^i ($i=0, 1, \dots, n-1$). Using these definitions in the n canonical equations [equation (30) for $D = D_i$ and $P = P^i$] we have transformed the set of n original relationships, equations (23) and (24), into the equivalent set of n following equations,

$$\begin{aligned} & -\rho \left\{ a_0^i \frac{dT^{-1}}{dt} + a_1^i \frac{d[(\mu_n - \mu_1)T^{-1}]}{dt} \right. \\ & \quad + \dots a_k^i \frac{d[(\mu_n - \mu_k)T^{-1}]}{dt} \\ & \quad \left. + a_{n-1}^i \frac{d[(\mu_n - \mu_{n-1})T^{-1}]}{dt} \right\} \\ & + \rho D_i \left\{ a_0^i \nabla^2 T^{-1} + a_1^i \nabla^2 [(\mu_n - \mu_1)T^{-1}] \right. \\ & \quad + \dots a_k^i \nabla^2 [(\mu_n - \mu_k)T^{-1}] \\ & \quad \left. + \dots a_{n-1}^i \nabla^2 [(\mu_n - \mu_{n-1})T^{-1}] \right\} - \rho \frac{D_i}{c_0^2} \\ & \times \left\{ a_0^i \frac{d^2 T^{-1}}{dt^2} + \dots a_k^i \frac{d^2 [(\mu_n - \mu_k)T^{-1}]}{dt^2} \right. \\ & \quad \left. + \dots a_{n-1}^i \frac{d^2 [(\mu_n - \mu_{n-1})T^{-1}]}{dt^2} \right\} = 0 \end{aligned} \tag{41}$$

$i = 0, 1, \dots, n-1$

each having the simple structure of equation (30). From this structure it will be very easy to formulate the variational principle on the basis of the results of Section 2.

5. THE VARIATIONAL PRINCIPLE FOR COUPLED HEAT AND MASS TRANSFER PROCESSES

Comparison of equations (3), (16) and (30) verifies the relevant functional for the processes of simultaneous heat and mass transfer described by normal potentials $P^0; P^1, P^{n-1}$:

$$S = \iiint \iiint \left\langle \sum_{i=0}^n \left\{ \rho D_i \left[(\text{grad } P^i)^2 - \left(\frac{dP^i}{dt} \right)^2 \frac{1}{c_0^2} \right] \right\} \right. \\ \left. \times \exp \left[\frac{c_0^2 t}{D_i} \right] \right\rangle d\Omega \tag{42}$$

since the condition $\delta S = 0$ leads to the set of relationships given by equation (30) for $P = P^0, P^1, \dots, P^{n-1}$. Returning now in integral (42) to the original transfer potentials, $T^{-1}, (\mu_n - \mu_1)T^{-1}$, etc. we obtain with the help of equation (31) for $P = P^i$ and $a_k = a_k^i$, the following functional:

$$S = \iiint \iiint \left\langle \sum_{i=0}^{n-1} \left\{ \rho D_i \left[\sum_{k=1}^3 \left(a_0^i \frac{\partial T^{-1}}{\partial x_k} \right. \right. \right. \right.$$

$$\begin{aligned} & \left. + a_1^i \frac{\partial [(\mu_n - \mu_1)T^{-1}]}{\partial x_k} \right] \dots \\ & \left. + \dots a_{n-1}^i \frac{\partial [(\mu_n - \mu_{n-1})T^{-1}]}{\partial x_k} \right)^2 \\ & - \frac{1}{c_0^2} \left(a_0^i \frac{dT^{-1}}{dt} + a_1^i \frac{d[(\mu_n - \mu_1)T^{-1}]}{dt} \dots \right. \\ & \left. + a_{n-1}^i \frac{d[(\mu_n - \mu_1)T^{-1}]}{dt} \right)^2 \Bigg\} \\ & \times \exp \left[\frac{c_0^2 t}{D_i} \right] \Bigg\rangle d\Omega \end{aligned} \tag{43}$$

the stationarity conditions of which are equation (41) or equations (23) and (24) for the transfer potentials constant at the boundaries of Ω .

All coefficients of this functional, i.e. a_j^i and D_i of equations (40) and (34) respectively, are known as they were obtained* from the elements of the two basic thermodynamic matrices, the thermostatic matrix C , equation (26), and the kinetic (Onsager's) matrix, equation (25). Thus we have obtained a well-defined classical functional leading to the set of equations describing non-stationary, coupled processes of energy and mass transfer.

6. DISCUSSION

If in the integral, equation (43), the terms with time derivatives and the exponential terms are disregarded, i.e. if the non-stationarity and convection effects are neglected, then in view of relations, equation (31) and equation (A.5), in the Appendix, the product of the total entropy source and the constant time interval Δt is obtained. The total entropy produced is then represented by S and the stationarity conditions, $\delta S = 0$, leads in such a case to the conclusion that, at the steady-state, the real spatial distribution of the transfer potential gradients makes the entropy source both stationary and minimal [1,4]. Euler's equations are then the classical equations of change taken for time-independent processes without convection. For that reason the stationarity principle $\delta S = 0$ for the functional S defined by equation (43) replaces the Prigogine's variational principle of the minimum entropy source† in those cases when the time-dependent heat and mass transfer occurs in which all three transport mechanisms, viz. by convection, diffusion and relaxation are of importance. It should be emphasized that the result obtained does not lead to the conclusion about the minimum of entropy source in the non-stationary processes considered.

* Remember that, in general, there is no explicit formula for the solution of every Eigenvalue problem. It is, however, possible to compute coefficients a_j^i and D_i in any concrete case in the manner described in Section 4.

† We consider here only the exact variational formulation exploiting the entropy production functional in stationary case and no other extremum formulations (related to this case) that can also be found in [4].

The principle of stationarity of functional S possesses all the advantages and shortcomings of Prigogine's variational principle. This is a general principle which accounts for the effects of all the transport mechanisms. On the other hand the principle is valid when ever the assumption of the constancy of macroscopic coefficients applies.

From the view point of heat and mass transfer specialists the practical usefulness of the variational principle given consists in finding approximate fields of temperature and chemical potentials (concentration fields can then be found) with the help of direct variational methods. As usual it is then assumed, that the solution $T^{-1}(x, y, z, t), \dots, (\mu_n - \mu_1)/T(x, y, z, t)$ etc. of the set of hyperbolic equations (23) and (24) may be represented everywhere by complete and linearly independent sets of functions* $\phi_T^l(x, y, z, t), \phi_{\mu 1}^l(x, y, z, t), \dots$ etc. We write

$$T^{-1} = \sum_{l=1}^p \alpha_T^l \phi_T^l(x, y, z, t);$$

$$\tilde{\mu}_1 T^{-1} = \sum_{l=1}^p \alpha_{\mu 1}^l \phi_{\mu 1}^l(x, y, z, t), \dots \text{etc} \quad (44)$$

where the $\{\alpha_T^l\}, \{\alpha_{\mu 1}^l\}, \dots$ are the n set of parameters. We then introduce the approximations, equation (44), into the functional (43) and perform its minimization with respect to the parameters as in the Rayleigh-Ritz method [11, 12]. We obtain in this way the optimal values of parameters leading to approximate expression for transfer potentials. The practical details of the above aspect of application will be the subject of a separate paper, where a computational sample of coefficients D_i, a_i^j and m_i^j will also be given

7. CONCLUSION AND SIGNIFICANCE

Variational principles of a classical type known previously for macroscopic systems are valid separately for either reversible or irreversible phenomena [1, 3]. For instant, the recognized least action principle [3] pertained to the first and the minimum entropy production principle, [1], to the second type of these phenomena. No classical type principles have been given for macroscopic processes in which the irreversible phenomena were accompanied by the reversible ones. Since in our real macroscopic world such particular processes generally prevail, the practical value of the principles mentioned previously was restricted and non-classical approaches as in the local potential method [4] have been advanced.

In this work a powerful method has been given for finding variational principles of classical type which apply to macroscopic processes with reversible and irreversible phenomena. This method leads to time-unsymmetrical and position-unsymmetrical Euler equations, due to the presence of non-autonomous exponential terms in the Lagrangian's of the func-

tionals, equations (16) and (43). Such equations conserve the fundamental irreversibility property, namely; the change in time sign or spatial co-ordinate sign does not lead to unchanged process picture, this is not so in the reversible process case.

To explain it more clearly let us consider the most simple example of the irreversible process when a solid sphere with mass m_s and diameter d falls vertically in quiescent viscous gas and the motion is laminar. It is sufficient to consider here this simple problem and we refer the reader to the previous work [15] for a more detailed analysis and generalizations. In the gas case the buoyancy and virtual mass effects can be neglected and the suitable functional is of the form:

$$S = \int_0^{t_f} m_s(\dot{z}^2 - gz) \exp\left(\frac{3\pi d \bar{\mu} t}{m_s}\right) dt \quad (45)$$

since the condition $\delta S = 0$ leads to the wellknown equation of motion

$$m_s \ddot{z} + 3\pi \bar{\mu} \dot{z} + m_s g = 0 \quad (46)$$

containing the Stokes expression for viscous force. The functional, equation (45), as well as the trajectory $z(t)$ of equation (46) change with transformation $t \rightarrow -t$ because of the presence of the exponential term in equation (45) resulting in appearance of the Stokes term in equation (46). If, however, the viscosity $\bar{\mu}$ of the fluid approaches zero then the exponential term of equation (45) approaches unity and the functional S reduces to the well-known least action functional [3]. Consequently the Stokes term in equation (46) vanishes and the trajectory of this equation does not change with $t \rightarrow -t$ as a trajectory of a microscopic world process. An analogue analysis is valid for the more complicated functionals (16) and (43) in Sections 1 and 6. Thus, due to the presence of exponential term in the integrands of equations (16), (43) and (45) the variational principles were found for more general processes in which irreversible phenomena are accompanied by reversible ones. The existence of the classical variational principles for such processes is of considerable theoretical importance for the fundamentals of irreversible thermodynamics and transport phenomena sciences.

From the view point of the heat and mass transfer specialists the practical value of this work should also be underlined. The functionals found make it possible to obtain the solutions of the transport equations by direct variational methods [11] with considerable accuracy, even in the case of complex boundary conditions (see e.g. Section 6 and numerical examples in [5 and 7]).

REFERENCES

1. S. R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics*. North Holland, Amsterdam (1962).
2. B. A. Finlayson and L. E. Scriven, On the search for variational principles, *Int. J. Heat Mass Transfer* **10**, 779-829 (1967).
3. V. Yourgrau and S. Mandelstam, *Variational Principles in Dynamics and Quantum Mechanics*, 2nd ed. Pitman,

* Each of which satisfies separately the boundary conditions.

- London (1960).
4. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*. Wiley, Interscience, London (1971).
 5. B. Vujanovic, An approach to linear and nonlinear heat transfer problem using a Lagrangian, *AIAA JI* **9**, 131–134 (1971).
 6. B. Vujanovic, D. Diukic and M. Pavlovich, A variational principle for the boundary layer theory, *Bull U.M.I.* **7**, 317–391 (1973).
 7. S. Sieniutycz, The variational principles of classical type for non-coupled non-stationary irreversible transport processes with convective motion and relaxation, *Int. J. Heat Mass Transfer* **20**, 1221–1231 (1977).
 8. S. Sieniutycz, The wave equations for simultaneous heat and mass transfer in moving systems—Structure testing time Space transformations and variational approach, *Int. J. Heat Mass Transfer* **22**, 585–599 (1979).
 9. G. Lebon, A new variational principle for the non-linear unsteady heat conduction problem, *Q. Jl Mech. Appl. Math.* **29**, 499–509 (1976).
 10. B. A. Finlayson, *The Method of Weighted Residuals and Variational Principles*. Academic Press, New York (1972).
 11. R. S. Schechter, *The Variational Method in Engineering*, McGraw-Hill, New York (1967).
 12. L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis*, trans. by C. D. Benster. Nordhoff, Groningen (1958).
 13. E. T. Whittaker, *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies with an Introduction to the Problem of Three Bodies*. Cambridge University Press (1952).
 14. B. Kowalczyk, *Matrices and Their Applications*. WNT, Warsaw (1976).
 15. S. Sieniutycz, The principle of stationary action for laminar motion of solids in viscous fluid, *Inzh. Chem.* **6**, 673–681 (1976) (in Polish).

APPENDIX

THE DIAGONALIZATION OF MATRICES AND QUADRATIC FORMS IN NORMAL COORDINATES P^i

Introducing vectors $\mathbf{Q} = \text{col}(T^{-1} - T_0^{-1}, (\mu_n - \mu_1)T^{-1} - (\mu_{n0} - \mu_{10})T^{-1}, \dots)$ $\mathbf{P} = \text{col}(P^0, P^1, \dots, P^{n-1})$ and matrix $\mathbf{M} = [\mathbf{m}^0, \mathbf{m}^1, \dots, \mathbf{m}^{n-1}]$ the column of which are the vectors \mathbf{m}^i one can write equations (38) and (39) in a common form

$$\mathbf{M}^T \mathbf{C} \mathbf{M} = -\mathbf{E} = \text{diag}(-1, -1, \dots, -1) \quad (\text{A.1})$$

where \mathbf{E} is unitary matrix. Also, since \mathbf{m}^i are solutions of equation (33) one has $\mathbf{L} \mathbf{m}^i = -D_j \rho \mathbf{C} \mathbf{m}^i$ and

$$(\mathbf{m}^i)^T \mathbf{L} \mathbf{m}^j = D_j (\mathbf{m}^i)^T (-\rho \mathbf{C}) \mathbf{m}^j \quad (\text{A.2})$$

for $i, j = 0, 1, \dots, n-1$.

Hence, from the definition of \mathbf{M} and using equations (A.1) and (A.2)

$$\mathbf{M}^T \mathbf{L} \mathbf{M} = \rho \tilde{\mathbf{D}} = \text{diag}(\rho D_0, \rho D_1, \dots, \rho D_{n-1}). \quad (\text{A.3})$$

One may see, that our orthonormality conditions, equations (38) and (39) in the text, resulted in simultaneous transfor-

mation of the two symmetric matrices \mathbf{C} and \mathbf{L} into the diagonal matrices, $\text{diag}(-1, -1, \dots, -1)$ and $\text{diag}(\rho D_0, \rho D_1, \dots, \rho D_{n-1})$, respectively. We shall show that it is associated with a diagonal form of the entropy production expressed in terms of potentials P^i and also with the diagonalization of other quadratic forms of interest. Indeed, for the transformations $\mathbf{Q} \rightarrow \mathbf{P}$, we have, from equations (31) and (32) for $i=0, 1, \dots, n-1$ and from equation (A.1) for symmetric \mathbf{C}

$$\mathbf{P} = (\mathbf{C} \mathbf{M})^T \mathbf{Q} = \mathbf{M}^T \mathbf{C} \mathbf{Q} = -\mathbf{M}^{-1} \mathbf{Q}. \quad (\text{A.4})$$

Hence $\mathbf{Q} = -\mathbf{M} \mathbf{P}$ and since \mathbf{M} is independent of time and position and equation (A.3) holds, the local entropy production written as

$$\sum_{s=1}^3 \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right)^T \mathbf{L} \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right)$$

transforms as follows

$$\begin{aligned} \sum_{s=1}^3 \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right)^T \mathbf{L} \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right) &= \sum_{s=1}^3 \left(-\mathbf{M} \frac{\partial \mathbf{P}}{\partial x_s} \right)^T \mathbf{L} \left(-\mathbf{M} \frac{\partial \mathbf{P}}{\partial x_s} \right) \\ &= \sum_{s=1}^3 \rho \left(\frac{\partial \mathbf{P}}{\partial x_s} \right)^T \tilde{\mathbf{D}} \left(\frac{\partial \mathbf{P}}{\partial x_s} \right) \\ &= \sum_{s=1}^3 \sum_{i=0}^{n-1} \rho D_i \left(\frac{\partial P^i}{\partial x_s} \right)^2 \end{aligned} \quad (\text{A.5})$$

By the same reasoning with the help of equation (A.1) one has

$$\begin{aligned} \mathbf{Q}^T \mathbf{C} \mathbf{Q} &= (-\mathbf{M} \mathbf{P})^T \mathbf{C} (-\mathbf{M} \mathbf{P}) \\ &= -\mathbf{P}^T \mathbf{P} = -\sum_{i=0}^{n-1} (P^i)^2. \end{aligned} \quad (\text{A.6})$$

Also

$$\dot{\mathbf{Q}}^T \mathbf{C} \dot{\mathbf{Q}} = -\sum_{i=0}^{n-1} (\dot{P}^i)^2 \quad (\text{A.7})$$

Similarly for some four-dimensional counterpart of entropy production, i.e. for generalization of the integrand of equation (6) in the multipotential case we have

$$\begin{aligned} \sum_{s=1}^3 \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right)^T \mathbf{L} \left(\frac{\partial \mathbf{Q}}{\partial x_s} \right) - \frac{1}{c_0^2} \left(\frac{d\mathbf{Q}}{dt} \right)^T \mathbf{L} \left(\frac{d\mathbf{Q}}{dt} \right) \\ = \sum_{i=0}^{n-1} \left\{ \rho D_i \left[(\text{grad } P^i)^2 - \left(\frac{dP^i}{dt} \right)^2 \frac{1}{c_0^2} \right] \right\}. \end{aligned} \quad (\text{A.8})$$

We may see that basic bilinear forms appearing in this work diagonalize in the normal co-ordinates P^i . This conclusion applied to the local entropy production bilinear form, equation (A.5), is used in Section 6 to show that the variational principle advanced here reduces to the minimum entropy production principle for the stationary case of the system at rest.

It may be also noted that the coefficients a_j^i appearing in our functional, equation (43), are elements of the matrix $(\mathbf{C} \mathbf{M})^T$. Since $(\mathbf{C} \mathbf{M})^T$ equals to \mathbf{M}^{-1} , cf. equation (A.1), the principal matrix of the Eigenvalue problem, \mathbf{M} , is the only quantity that is necessary to find the coefficients a_j^i .

**LE PRINCIPE VARIATIONNEL REMPLACANT LE PRINCIPE DE
PRODUCTION MINIMALE D'ENTROPIE POUR UN PROCESSUS
INSTATIONNAIRE DE TRANSFERT DE CHALEUR ET DE MASSE AVEC
MOUVEMENT CONVECTIF ET RELAXATION**

Résumé—On sait [1] que le théorème variationnel de la production minimale d'entropie ne s'applique pas aux mécanismes instationnaires en présence ou non de convection. Dans de tels cas une nouvelle fonctionnelle thermodynamique du type de Hamilton remplace la fonctionnelle de production d'entropie. Les conditions de stationnarité de cette fonctionnelle sont les équations hyperboliques du transport couplé d'énergie et de masse qui prennent en compte les effets de non stationnarité et de mouvement macroscopique en équilibre mécanique.

La conséquence pratique du principe variationnel donné est de trouver des champs approchés de température et de concentration à l'aide des méthodes variationnelles directes.

**ERSATZ DES PRINZIPI DER MINIMALEN ENTROPIEZUNAHME DURCH
DAS VARIATIONSPRINZIP BEI GEKOPPELTEM- INSTATIONÄREN
WÄRME- UND STOFFÜBERGANG MIT KONVEKTIVER BEWEGUNG UND
RELAXATION**

Zusammenfassung—Es ist bekannt [1], daß das Variationstheorem der minimalen Entropiezunahme nicht für instationäre Prozesse und/oder bei Auftreten von Konvektion angewendet werden kann. Für derartige Prozesse wird in dieser Arbeit ein neues thermodynamisches Funktional vom Hamilton-Typ angegeben, das das Funktional der Entropiezunahme ersetzt. Im stationären Fall hat das Funktional die Form der hyperbolischen Gleichungen für gekoppelten Energie- und Massentransport, welche die Effekte der instationären und makroskopischen Bewegung bei mechanischem Gleichgewicht berücksichtigen. Die praktische Bedeutung des angegebenen Variationsprinzips besteht darin, mittels direkter Variationsmethoden Näherungslösungen für Temperatur- und Konzentrationsverteilung ermitteln zu können.

**ИСПОЛЬЗОВАНИЕ ВАРИАЦИОННОГО ПРИНЦИПА ВМЕСТО ПРИНЦИПА
МИНИМАЛЬНОГО ПРИРОСТА ЭНТРОПИИ ДЛЯ СВЯЗАННЫХ НЕСТАЦИОНАРНЫХ
ПРОЦЕССОВ ТЕПЛО- И МАССОПЕРЕНОСА ПРИ КОНВЕКЦИИ И РЕЛАКСАЦИИ**

Аннотация— Хорошо известно, что вариационную теорему о минимальном производстве энтропии нельзя использовать для описания нестационарных процессов, если к тому же имеет место конвекция. Для таких процессов вместо функционала производства энтропии в данной работе предлагается новый термодинамический функционал гамильтоновского типа, стационарными условиями для которого являются гиперболические уравнения взаимосвязанного переноса энергии и массы, учитывающие эффекты нестационарности и макроскопического движения при механическом равновесии.

Практическая значимость предлагаемого вариационного принципа заключается в возможности нахождения приближенных температурных и концентрационных полей прямыми вариационными методами.