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THERMODYNAMICS OF IRREVERSIBLE PROCESSES AND DERIVATION OF A SYSTEM OF DIFFERENTIAL EQUATIONS FOR MOLECULAR TRANSFER

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On the basis of the linear laws of the thermodynamics of irreversible processes and the law of conservation of matter, a system of differential equations is derived for molecular transfer in the presence of n interrelated flows of generalized charges.

The current theory of transfer of generalized charges within a capillary-porous medium makes wide use of the methods of the thermodynamics of irreversible processes.

It is well known that the thermodynamics of irreversible processes is based on two principles: the linear law and the Onsager reciprocity relation. A large number of irreversible processes is known, the laws of which are expressed phenomenologically by linear relations between cause and effect. According to the linear law, the rate I (effect) of approach of the system to the equilibrium state is proportional to the thermodynamic motive force X (cause), which in turn may be expressed in terms of a potential gradient. Examples are heat conduction, giving heat flux proportional to temperature gradient $(I=-\lambda \operatorname{grad} T)$ diffusion, giving the flux of a mixture component proportional to concentration gradient $(I_m=-\lambda_m \operatorname{grad} U)$, Ohm's law, giving current density proportional to potential gradient $(I=-\sigma \operatorname{grad} \varphi)$, etc.

These linear laws have been the basis for the derivation of the corresponding differential equations (heat conduction, diffusion, electrical conduction, etc.).

In contrast to the classical situation for transfer of heat, mass of bound substance, electrical charges, etc., based on which the corresponding differential equations were derived, we are now concerned with the use of the thermodynamics of irreversible processes.

While previously in the study of transfer of heat, electricity and mass of bound substance, the independent linear transfer equations were examined, we now assume the initial transfer equations to be a set of linear Onsager equations, in which any given type of transfer is determined by the action of a direct effect and of the concurrent transfer phenomena. Mathematically, the effects of superposition are described by additional terms in the basic transfer law (direct effect). These linear Onsager equations lead to a system of interdependent differential equations of molecular transfer—to a system of partial differential equations of parabolic type relating to the potential fields of distribution of temperature, electricity and mass of bound substance, etc.

According to the linear law, the flux I_i resulting from the action of n generalized forces X_k $(k = 1, 2, \ldots n)$ is proportional to these forces:

$$I_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots n). \tag{1}$$

The quantity L_{ik} is called the phenomenological (kinetic) Onsager coefficient. The diagonal coefficients L_{kk} give the transfer intensity of the k-th generalized charge under the action of the like force X_k. The coefficients L_{ik} when $i \neq k$ are called entrainment coefficients and are connected with the superposed phenomena.

The Onsager reciprocity relation establishes that, with appropriate choice of fluxes I_i and forces X_i, the matrix composed of the kinetic coefficients

$$\begin{vmatrix} L_{11} & L_{12} & \ldots & L_{1n} \\ L_{21} & L_{22} & \ldots & L_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ L_{n1} & L_{n2} & \ldots & L_{nn} \end{vmatrix}, \tag{2}$$

is symmetric, i.e.,

$$L_{ik} = L_{ki}. \tag{3}$$

This relation results from microscopic reversibility.

For instance, in the case of nonisothermal diffusion and heat conduction within a porous medium, we may write

$$I_1 = L_{11}X_1 + L_{12}X_2,$$
$$I_2 = L_{21}X_1 + L_{22}X_2, \tag{4}$$

where I_1 is the energy (heat) flux; I_2 is the mass flux of bound substance. L_{21}, L_{12} establish the relation between the superposed phenomena (thermal diffusion, i.e., temperature gradient, causes mass transfer, and diffusion heat conduction, i.e., concentration gradient, causes heat transfer). L_{12} is proportional to the Soret coefficient, and L_{21} to the Dufour coefficient.

The equality of nondiagonal kinetic coefficients $L_{12} = L_{21}$ indicates symmetry between the influence of the diffusion force on heat flow and the influence of the thermal force on the mass flux. To clarify the quantitative interaction of the various fluxes, we shall differentiate the linear equations of system (4)

$$\left(\frac{\partial I_1}{\partial X_2}\right)_{X_1} = L_{12}, \quad \left(\frac{\partial I_2}{\partial X_1}\right)_{X_2} = L_{21}. \tag{5}$$

From the reciprocity relation (3) we obtain

$$\partial I_1/\partial X_2 = \partial I_2/\partial X_1. \tag{6}$$

The increment of energy (heat) flux, referred to unit increment of kinetic force X_2 (gradient of the bound mass distribution) is equal to the increment of mass flux, referred to unit increment of kinetic force X_1 (temperature gradient).

To derive the system of differential equations of molecular transfer, we shall make certain assumptions regarding the model of the thermodynamic system in which the transfer process occurs. We shall suppose that within an isotropic capillary-porous body (conductor), there are n generalized charges. These are transferred under the influence of n generalized forces $X_1, X_2, \ldots, X_n$, whose potentials are $U_1(x, y, z, t)$, $U_2(x, y, z, t), \ldots\ldots, U_n(x, y, z, t)$. Thus, the thermodynamic system is really heterogeneous and is assumed to be continuous, i.e., any volume element of the conductor is filled by all n components of the generalized charges.

We shall write the generalized forces $X_1, X_2, \ldots, X_n$ in terms of the gradients of the corresponding potentials

$$X_k = -\nabla U_k = -\operatorname{grad} U_k.$$

Under these conditions the linear equations (1) may be written in the form

$$I_k = -(L_{k1}\nabla U_1 + L_{k2}\nabla U_2 + \ldots + L_{kn}\nabla U_n)$$
$$(k = 1, 2, \ldots n). \tag{7}$$

Let us examine a volume element of V inside the conducting body (conductor) bounded by the surface S, and divide the surface S into m arbitrary parts. Let ΔS_i be the area of the i-th part of S; then $\Delta E_{ki} = I_k(p_i', t)\Delta S_i$ is the amount of the k-th generalized charge passing through ΔS_i in unit time, while $(E_k)_m = \sum_{i=1}^{m} \Delta E_{ki} = \sum_{i=1}^{m} I_k(p_i'; t)\Delta S_i$ is the approximate value of the total generalized charge passing through the whole surface S in unit time t. Hence $E_k = \lim_{m\to\infty} \sum_{i=1}^{m} I_k(p_i', t)\Delta S_i = \iint_S I_k(p', t)\,dS$ is the amount of generalized charge of the k-th flux passing through the control surface S in unit time. The integral here is taken over the whole surface S of volume V.

In the absence of sources to excite the k-th generalized charge within volume V, the flux through surface S causes a change in the charge content amounting to $\iiint_{(V)} \gamma C_k \frac{\partial U_k}{\partial t}\,dV$.

On the basis of the law of conservation of matter, the change of charge content in volume V equals its loss through surface S bounding the given volume V, i.e.,

$$-\iiint_{(V)} \frac{\partial U_k}{\partial t}\gamma C_k dV = \iint_S I_k(p', t)\,dS. \tag{8}$$

Substituting the value of $I_k(p', t)$ according to (7), we obtain

$$\iiint_{(V)} \gamma C_k \frac{\partial U_k}{\partial t}\,dV = \iint_S \left[\sum_{i=1}^{n} L_{ki}\operatorname{grad} U_i\right] dS. \tag{9}$$

Making use of M. V. Ostrogradskii's formula, we express the double integral over surface S in terms of a triple integral over volume V:

$$\iint\limits_S \left[\sum_{i=1}^{n} L_{ki} \operatorname{grad} U_i\right] dS = \iiint\limits_{(V)} \operatorname{div} \left[\sum_{i=1}^{n} L_{ki} \operatorname{grad} U_i\right] dV. \tag{10}$$

The equality (9) takes the form

$$\iiint\limits_{(V)} \gamma C_k \frac{\partial U_k}{\partial t} dV = \iiint\limits_{(V)} \operatorname{div} \left[\sum_{i=1}^{n} L_{ki} \operatorname{grad} U_i\right] dV. \tag{11}$$

Since (11) has been obtained for any arbitrary volume V, it follows that

$$\gamma C_k \frac{\partial U_k}{\partial t} = \operatorname{div} \left[\sum_{i=1}^{n} L_{ki} \operatorname{grad} U_i\right] \tag{12}$$

$$(k = 1,\ 2,\ \ldots,\ n).$$

System (12) is a system of differential equations for transfer in the presence of n interrelated fluxes of generalized charges.

If L_{ki} does not depend on the coordinates of a point in space, (12) is considerably simplified:

$$\frac{\partial U_k}{\partial t} = \sum_{i=1}^{n} a_{ki}^2 \nabla^2 U_i, \tag{13}$$

where

$$\nabla^2 U = \operatorname{div}(\operatorname{grad} U),\quad a_{ki}^2 = L_{ki}/\gamma C_k \geqslant 0.$$

Within the conductor let there be sources creating generalized charges of specific powers $W_1(x,\ y,\ z,\ t)$, $W_2\ (x,\ y,\ z,\ t),\ \ldots,\ W_n(x,\ y,\ z,\ t)$; then (13) takes the form

$$\begin{aligned} \frac{\partial U_1}{\partial t} &= a_{11}^2 \nabla^2 U_1 + a_{12}^2 \nabla^2 U_2 + \ldots + a_{1n}^2 \nabla^2 U_n + \theta_1(x,\ y,\ z,\ t), \\ \frac{\partial U_2}{\partial t} &= a_{21}^2 \nabla^2 U_1 + a_{22}^2 \nabla^2 U_2 + \ldots + a_{2n}^2 \nabla^2 U_n + \theta_2(x,\ y,\ z,\ t), \\ &\ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \\ &\ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots, \\ \frac{\partial U_n}{\partial t} &= a_{n1}^2 \nabla^2 U_1 + a_{n2}^2 \nabla^2 U_2 + \ldots + a_{nn}^2 \nabla^2 U_n + \theta_n(x,\ y,\ z,\ t), \end{aligned} \tag{14}$$

where

$$\theta_k = W_k/C_k \gamma.$$

Here as before the reciprocal Onsager relations

$$\gamma C_k a_{ki}^2 = \gamma C_i a_{ik}^2 \tag{15}$$

must be valid.

The set of differential equations of molecular transfer (14), together with the Onsager relations (15), describe mathematically the law of variation of potential functions of distribution of generalized charges with account for flux interaction.

Analytical solutions of boundary value problems for various initial boundary conditions in the system of differential equations of parabolic type (14) are of interest in general transfer theory. Methods of solution of boundary value problems for (14), and analysis of these solutions expressed in dimensionless form, lead to new ways of experimental and theoretical investigation of the mechanism of heat and mass transfer.

Whereas in investigations of heat and mass transfer, the thermodynamics of irreversible processes permits us, through the agency of its phenomenological laws, to take into account certain qualitative laws observed experimentally and to obtain the fundamental effects from them, analytical solutions of the system now enable us to treat the quantitative aspects of transfer.

Thus, analytical methods of the thermodynamics of irreversible processes, methods of statistical physics, and mathematical methods of solving the boundary value problem for system (14) may be combined together in a general experimental and theoretical investigation of the mechanism of heat and mass transfer.

A number of new boundary value problems for the system of differential equations of transfer has been solved and published. A method has been described by M. S. Smirnovyi [1, 2] for reducing the boundary value problem for a system of differential equations relating to drying to the solution of the corresponding boundary value problem for a differential equation of the heat conduction type. This method considerably simplifies the complex solution of the basic boundary value problem and gives some new quantitative relations. In particular, Eq. (20) of [1] enables us to obtain the drying rate from the heat transfer rate by simple differentiation.

The author of [3, 4] solved some boundary value problems for (14) by reducing a system of n differential equations of parabolic type to the inhomogeneous heat conduction type of equation. This method is, in essence, a generalization of the D'Alembert method.

NOTATION

I_k—flux of k-th generalized charge; X—generalized force; U_k—scalar potential of generalized force X_k; L_{ik}—phenomenological Onsager coefficients; V—volume element of conductor; S—surface area of volume V or of control surface; p'—arbitrary point on surface S; E—quantity of generalized charge; γ—specific weight of conductor; C_k—specific mass capacity of material of conducting body (conductor) with respect to k-th generalized charge; a^2_{kk}—potential conductivity of k-th generalized charge; Δ—Hamiltonian operator.

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