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THE RECIPROCITY PRINCIPLE IN THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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The phenomenological basis of the reciprocity principle is described, and the transfer of mass and energy in a multicomponent medium is examined as an example.

The linear law and the Onsager reciprocity principles are new principles of the thermodynamics of irreversible processes. The linear law was examined in [1]. The present paper sets out some considerations related to the Onsager reciprocity principle.

This principle states that with appropriate choice of fluxes and forces, the matrix of kinetic coefficients is symmetric, i.e.,

$$L_{ik} = L_{ki} \quad (i,\ k = 1,\ 2 \ldots n) \tag{1}$$

These equalities specify a relation between the irreversible processes occurring in nonequilibrium systems.

The proof of (1) is based on considerations of statistical mechanics, including the principle of microscopic reversibility.

The application of the method of statistical mechanics to the phenomenological relations is not logically necessary, since the reciprocity principle should be considered to be essentially phenomenological and should be based on phenomenological considerations. It is shown below that the reciprocity principle is based on the mutual relation between the quantities determining compatible irreversible processes.

To obtain a phenomenological basis for the reciprocity principle, it is necessary to examine the transfer of mass and energy in a multi-component medium.

Let us take a complex n-component medium in an unsteady, nonequilibrium change of state process which is close to steady. Let the partial mass and energy densities of components of the medium have the values $\rho_{11}, \rho_{22}, \ldots, \rho_{nn}$ and $\varepsilon_{11}, \varepsilon_{22}, \ldots, \varepsilon_{nn}$. These values will be functions of the space coordinates and of time.

An unsteady, nonequilibrium change of state process in a n-component medium is characterized by n basic mass transfer vectors for the medium components and n basic energy transfer vectors.

These basic vectors are given by the expressions

$$\mathbf{q}_{\text{м}11} = -a_{\text{м}11}\,\text{grad}\,\rho_{11}, \quad \mathbf{q}_{\text{э}11} = -a_{\text{э}11}\,\text{grad}\,\varepsilon_{11},$$
$$\mathbf{q}_{\text{м}22} = -a_{\text{м}22}\,\text{grad}\,\rho_{22}, \quad \mathbf{q}_{\text{э}22} = -a_{\text{э}22}\,\text{grad}\,\varepsilon_{22},$$
$$\ldots\ldots\ldots\ldots \quad \ldots\ldots\ldots\ldots,$$
$$\mathbf{q}_{\text{м}nn} = -a_{\text{м}nn}\,\text{grad}\,\rho_{nn}, \quad \mathbf{q}_{\text{э}nn} = -a_{\text{э}nn}\,\text{grad}\,\varepsilon_{nn}.$$

Strictly speaking, these expressions are valid when the mean thicknesses of equilibrium layers of the components (mean values of the mass and energy free path of components of the medium) are equal or at least commensurate.

Due to interaction, the basic mass and energy flux of each component of the medium entrains a finite amount of mass and energy from the other components in such a way that the moving composite n-component medium may be represented as consisting of n media, each made up of components occurring in definite proportions. We shall call these n media simple media components of the composite medium.

The partial mass and energy densities in the simple medium of the first component have values $\rho_{11}, \rho_{21}, \ldots, \rho_{n1}$, and $\varepsilon_{11}, \varepsilon_{21}, \ldots \varepsilon_{n1}$; in that of the second component – $\rho_{12}, \rho_{22}, \ldots, \rho_{n2}$ and $\varepsilon_{12}, \varepsilon_{22}, \ldots, \varepsilon_{n2}$, and in that of the nth component $\rho_{1n}, \rho_{2n}, \ldots, \rho_{nn}$ and $\varepsilon_{1n}, \varepsilon_{2n}, \ldots, \varepsilon_{nn}$.

Let us take the simple medium of the first component. The basic mass flux in this medium is

$$\mathbf{q}'_{\text{м}11} = -a_{\text{м}11}\,\text{grad}\,\rho_{11}.$$

This flux entrains definite amounts of the other components of the medium and creates secondary fluxes given by

$$\mathbf{q}'_{\text{м}21} = -a_{11}\frac{\rho_{21}}{\rho_{11}}\,\text{grad}\,\rho_{11},$$
$$\ldots\ldots\ldots\ldots\ldots\ldots,$$

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$$\mathbf{q}'_{Mn1} = -a_{11} \frac{\rho_{n1}}{\rho_{11}} \operatorname{grad} \rho_{11}.$$

The total mass transfer vector in the simple medium of the first component will be

$$\mathbf{q}'_{M1} = \mathbf{q}'_{M11} + \mathbf{q}'_{M21} + \ldots + \mathbf{q}'_{Mn1},$$

or

$$\mathbf{q}'_{M1} = -a_{11} \frac{\rho_{11} + \rho_{21} + \ldots + \rho_{n2}}{\rho_{11}} \operatorname{grad} \rho_{11}. \tag{2}$$

This vector may be calculated from the secondary flux of the second component, taking this secondary flux as the basic flux. The new basic flux, determined by the equality $\mathbf{q}'_{M21} = -a_{21} \operatorname{grad} \rho_{21}$, creates secondary fluxes of the other components, for which the expressions

$$\mathbf{q}'_{M11} = -a_{21} \frac{\rho_{11}}{\rho_{21}} \operatorname{grad} \rho_{21},$$

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$$\mathbf{q}'_{Mn1} = -a_{21} \frac{\rho_{n1}}{\rho_{21}} \operatorname{grad} \rho_{21}$$

will be valid.

Therefore,

$$\mathbf{q}'_{M} = -a_{21} \frac{\rho_{11} + \rho_{21} + \ldots + \rho_{n1}}{\rho_{21}} \operatorname{grad} \rho_{21}$$

Calculating $\mathbf{q}'_{M}$ from the flux of the nth component, we have

$$\mathbf{q}'_{M} = -a_{n1} \frac{\rho_{11} + \rho_{21} + \ldots + \rho_{n1}}{\rho_{n1}} \operatorname{grad} \rho_{n1}.$$

Let us suppose that the partial mass densities in the simple medium of the first component are related by

$$\rho_{21} = \varphi_{21}(\rho_{11}); \; \ldots ; \; \rho_{n1} = \varphi_{n1}(\rho_{11}).$$

Hence it follows that

$$\operatorname{grad} \rho_{21} = \varphi'_{21} \operatorname{grad} \rho_{11},$$

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$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \,,$$

$$\operatorname{grad} \rho_{n1} = \varphi'_{n1} \operatorname{grad} \rho_{11},$$

which gives

$$\mathbf{q}'_{M} = -a_{21} \frac{\rho_{11} + \rho_{21} + \ldots + \rho_{n1}}{\rho_{21}} \varphi'_{21} \operatorname{grad} \rho_{11}$$

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$$\mathbf{q}'_{M} = -a_{n1} \frac{\rho_{11} + \rho_{21} + \ldots + \rho_{n1}}{\rho_{n1}} \varphi'_{n1} \operatorname{grad} \rho_{11}.$$

Comparing each of these expressions with (2), we obtain

$$\begin{aligned} \frac{a_{11}}{\rho_{11}} &= \frac{a_{21}}{\rho_{21}} \varphi'_{21}, \\ . \quad . \quad . \quad . \quad &. \quad . \quad . \quad . \quad . \quad . \quad . \,, \\ . \quad . \quad . \quad . \quad &. \quad . \quad . \quad . \quad . \quad . \,, \\ \frac{a_{11}}{\rho_{11}} &= \frac{a_{n1}}{\rho_{n1}} \varphi'_{n1}. \end{aligned} \tag{3}$$

These equalities also determine the relation between mass transfer coefficients in the simple medium of the first component.

Similar equalities will determine the relation between mass transfer coefficients in the simple medium of the other components.

Reasoning analogous to the above allows us to write the following expressions for the total energy transfer vectors in the simple medium of the first component:

$$\mathbf{q}'_э = -a_{э11}\frac{\varepsilon_{11}+\varepsilon_{21}+\ldots+\varepsilon_{n1}}{\varepsilon_{11}}\operatorname{grad}\varepsilon_{11},$$

$$\mathbf{q}'_э = -a_{э21}\frac{\varepsilon_{11}+\varepsilon_{21}+\ldots+\varepsilon_{n1}}{\varepsilon_{21}}\operatorname{grad}\varepsilon_{21},$$

$$\cdots\cdots\cdots\cdots,$$

$$\cdots\cdots\cdots\cdots,$$

$$\mathbf{q}'_э = -a_{эn1}\frac{\varepsilon_{11}+\varepsilon_{21}+\ldots+\varepsilon_{n1}}{\varepsilon_{n1}}\operatorname{grad}\varepsilon_{n1}.$$

If we assume that the partial energy densities are connected by relations $\varepsilon_{21} = \psi_{21}(\varepsilon_{11}); \ldots; \varepsilon_{n1} = \psi_{n1}(\varepsilon_{11})$, we may obtain the following relations between energy transfer coefficients in the simple medium of the first component:

$$\frac{a_{э11}}{\varepsilon_{11}} = \frac{a_{э21}}{\varepsilon_{21}}\psi'_{21},$$
$$\cdots\cdots\cdots, \tag{4}$$
$$\frac{a_{э11}}{\varepsilon_{11}} = \frac{a_{эn1}}{\varepsilon_{n1}}\psi'_{n1}.$$

Similar relations may be written for the simple medium of the other components.

Relations (3) and (4) and their analogs are a mathematical expression of the reciprocity principle in simple media.

We shall calculate the total vector of the first component in the composite medium, i. e., in the n simple media of the components of the composite medium. The flux of the first component in the simple medium of this component is basic and is given by the expression

$$q_{м11} = a_{м11}\operatorname{grad}\rho_{11}.$$

The basic flux of the second component in the simple medium of this same component creates a secondary flux of the first component, given by the expression

$$q_{м12} = -a_{22}\frac{\rho_{12}}{\rho_{22}}\operatorname{grad}\rho_{22}.$$

For the secondary flux of the first component in the simple medium of the n-th component, the equality

$$\mathbf{q}_{м1n} = -a_{nn}\frac{\rho_{1n}}{\rho_{nn}}\operatorname{grad}\rho_{nn}$$

will be valid.

The total mass transfer vector of the first component of the composite medium is given by

$$\mathbf{q}_{м1} = \mathbf{q}_{м11} + \mathbf{q}_{м12} + \ldots + \mathbf{q}_{м1n},$$

or

$$\mathbf{q}_{м1} = -a_{м11}\operatorname{grad}\rho_{11} - a_{м22}\frac{\rho_{12}}{\rho_{22}}\operatorname{grad}\rho_{22} - \ldots$$
$$\ldots - a_{мnn}\frac{\rho_{1n}}{\rho_{nn}}\operatorname{grad}\rho_{nn}. \tag{5}$$

For the total mass transfer vectors of the other components, we may clearly write the equalities

$$\mathbf{q}_{м2} = -a_{м11}\frac{\rho_{21}}{\rho_{11}}\operatorname{grad}\rho_{11} - a_{м22}\operatorname{grad}\rho_{22} - \ldots$$
$$\ldots - a_{мnn}\frac{\rho_{2n}}{\rho_{2n}}\operatorname{grad}\rho_{nn}, \tag{6}$$
$$\cdots\cdots\cdots\cdots,$$

(contd)

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$$\mathbf{q}_{\text{м}n} = -a_{\text{м}11}\frac{\rho_{n1}}{\rho_{11}}\operatorname{grad}\rho_{11} - a_{\text{м}22}\frac{\rho_{n2}}{\rho_{22}}\operatorname{grad}\rho_{22} - \ldots - a_{\text{м}nn}\operatorname{grad}\rho_{nn}. \tag{6 (contd)}$$

Arguments analogous to the foregoing allow us to write the following expressions for the total energy transfer vectors of the components of the composite medium:

$$\begin{aligned}
\mathbf{q}_{\text{э}1} &= -a_{\text{э}11}\operatorname{grad}\varepsilon_{11} - a_{\text{э}22}\frac{\varepsilon_{11}}{\varepsilon_{22}}\operatorname{grad}\varepsilon_{22} - \ldots \\
&\quad \ldots - a_{\text{э}nn}\frac{\varepsilon_{1n}}{\varepsilon_{nn}}\operatorname{grad}\varepsilon_{nn}, \\
\mathbf{q}_{\text{э}2} &= -a_{\text{э}11}\frac{\varepsilon_{12}}{\varepsilon_{11}}\operatorname{grad}\varepsilon_{11} - a_{\text{э}22}\operatorname{grad}\varepsilon_{22} - \ldots \\
&\quad \ldots - a_{\text{э}nn}\frac{\varepsilon_{2n}}{\varepsilon_{nn}}\operatorname{grad}\varepsilon_{nn}, \\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \\
\mathbf{q}_{\text{э}n} &= -a_{\text{э}11}\frac{\varepsilon_{n1}}{\varepsilon_{11}}\operatorname{grad}\varepsilon_{11} - a_{\text{э}22}\frac{\varepsilon_{n2}}{\varepsilon_{22}}\operatorname{grad}\varepsilon_{22} - \ldots \\
&\quad \ldots - a_{\text{э}nn}\operatorname{grad}\varepsilon_{nn}.
\end{aligned} \tag{7}$$

These considerations may be extended to the process of transfer by the medium of a quantity u.

Let a composite n-component medium transfer n quantities: $u_{11}, u_{22}, \ldots, u_{nn}$. The basic transfer vectors will be determined by the expressions: $-a_{u11}\operatorname{grad}u_{11}, -a_{u22}\operatorname{grad}u_{22}, \ldots, -a_{unn}\operatorname{grad}u_{nn}$, where $u_{11}, u_{22}, \ldots, u_{nn}$ are the densities of the quantities transferred by the medium.

The total transfer vectors of the quantities concerned will be

$$\begin{aligned}
\mathbf{q}_{u1} &= -a_{u11}\operatorname{grad}u_{11} - a_{u22}\frac{u_{21}}{u_{22}}\operatorname{grad}u_{22} - \ldots \\
&\quad \ldots - a_{unn}\frac{u_{1n}}{u_{nn}}\operatorname{grad}u_{nn}, \\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \\
\mathbf{q}_{nn} &= -a_{u11}\frac{u_{n1}}{u_{11}}\operatorname{grad}u_{11} - a_{u22}\frac{u_{n2}}{u_{22}}\operatorname{grad}u_{22} - \\
&\quad - a_{unn}\operatorname{grad}u_{nn}.
\end{aligned} \tag{8}$$

We divide the composite n-component medium, which is in an unsteady nonequilibrium change of state process, into equilibrium volumes, and examine the movement of the composite medium in one of these volumes.

Let us take the i-th and k-th components of the medium.

Let these components be transformed from one into the other during the motion of the medium. This transformation causes specific changes of mass density of both components in their simple media according to the equations

$$\frac{\partial\rho_{ii}}{\partial\tau} + \frac{\partial\rho_{ki}}{\partial\tau} = 0, \tag{9}$$

$$\frac{\partial\rho_{kk}}{\partial\tau} + \frac{\partial\rho_{ik}}{\partial\tau} = 0. \tag{10}$$

The transformation causes the following specific change of the stereochrone of the medium:

$$\frac{1}{\rho_{ii}} \frac{\partial \rho_{ii}}{\partial \tau} + \frac{1}{\rho_{ki}} \frac{\partial \rho_{ki}}{\partial \tau} + \frac{1}{\rho_{kk}} \frac{\partial \rho_{kk}}{\partial \tau} + \frac{1}{\rho_{ik}} \frac{\partial \rho_{ik}}{\partial \tau}. \tag{11}$$

The volume of the disappearing amount of the i-th component in this simple medium is equal to $\frac{1}{\rho_{ii}} \frac{\partial \rho_{ii}}{\partial \tau}$.

If this volume is multiplied by the mass density of the k-th component in the simple medium of the i-th component, we obtain the specific mass of the k-th component appearing.

On this basis we may write

$$\frac{1}{\rho_{ii}} \frac{\partial \rho_{ii}}{\partial \tau} \rho_{ki} = \frac{\partial \rho_{ki}}{\partial \tau}$$

or

$$\frac{1}{\rho_{ii}} \frac{\partial \rho_{ii}}{\partial \tau} = \frac{1}{\rho_{ki}} \frac{\partial \rho_{ki}}{\partial \tau}. \tag{12}$$

From similar reasoning we obtain the equality

$$\frac{1}{\rho_{kk}} \frac{\partial \rho_{kk}}{\partial \tau} = \frac{1}{\rho_{ik}} \frac{\partial \rho_{ik}}{\partial \tau}. \tag{13}$$

Equalities (12) and (13) allow us to write (11) as follows:

$$\frac{2}{\rho_{ki}} \frac{\partial \rho_{ki}}{\partial \tau} + \frac{2}{\rho_{ik}} \frac{\partial \rho_{ik}}{\partial \tau},$$

or, taking (9) and (10) into account,

$$-\left(\frac{2}{\rho_{ki}} \frac{\partial \rho_{ii}}{\partial \tau} + \frac{2}{\rho_{ik}} \frac{\partial \rho_{kk}}{\partial \tau} \right).$$

The transfer vectors of the components of the medium in question are given by the expressions

$$\mathbf{q}_{Mi} = -a_{Mii} \operatorname{grad} \rho_{ii} - a_{Mkk} \frac{\rho_{ik}}{\rho_{kk}} \operatorname{grad} \rho_{kk}, \tag{14}$$

$$\mathbf{q}_{Mk} = -a_{Mii} \frac{\rho_{ki}}{\rho_{ii}} \operatorname{grad} \rho_{ii} - a_{Mkk} \operatorname{grad} \rho_{kk}. \tag{15}$$

The specific change of the medium stereochrone due to transfer of the components will be

$$\operatorname{div} \left(-\frac{a_{Mii}}{\rho_{ii}} \operatorname{grad} \rho_{ii} - a_{Mkk} \frac{\rho_{ik}}{\rho_{kk}\rho_{ik}} \operatorname{grad} \rho_{kk} - a_{Mii} \frac{\rho_{ki}}{\rho_{ii}\rho_{ki}} \operatorname{grad} \rho_{ii} - \frac{a_{Mkk}}{\rho_{kk}} \operatorname{grad} \rho_{kk} \right)$$

or

$$-2 \operatorname{div} \left(\frac{a_{Mii}}{\rho_{ii}} \operatorname{grad} \rho_{ii} + \frac{a_{Mkk}}{\rho_{kk}} \operatorname{grad} \rho_{kk} \right).$$

Since the medium is in the equilibrium state in the equilibrium volume, the total specific change of the medium stereochrone will be zero, i. e.,

$$\frac{1}{\rho_{ki}} \frac{\partial \rho_{ii}}{\partial \tau} + \frac{1}{\rho_{ik}} \frac{\partial \rho_{kk}}{\partial \tau} + \operatorname{div} \left(\frac{a_{Mii}}{\rho_{ii}} \operatorname{grad} \rho_{ii} + \frac{a_{Mkk}}{\rho_{kk}} \operatorname{grad} \rho_{kk} \right) = 0. \tag{16}$$

For the equilibrium volume we may write the equation

$$\frac{a_{Mii}}{\rho_{ii}} \operatorname{grad} \rho_{ii} + \frac{a_{Mkk}}{\rho_{kk}} \operatorname{grad} \rho_{kk} = 0. \tag{17}$$

Using (17), (16) may be written as

$$\frac{1}{\rho_{ki}}\frac{\partial \varphi_{ii}}{\partial \tau}+\frac{1}{\rho_{ik}}\frac{\partial \rho_{kk}}{\partial \tau}=0. \tag{18}$$

Assuming that the relation $\rho_{kk} = \varphi(\rho_{ii})$ exists, we have

$$\operatorname{grad}\rho_{kk}=\varphi'\operatorname{grad}\rho_{ii},$$

$$\frac{\partial \rho_{kk}}{\partial \tau}=\varphi'\frac{\partial \rho_{ii}}{\partial \tau},$$

which allows us to write (17) and (18) in the form

$$\frac{a_{\text{M}ii}}{\rho_{ii}}+\frac{a_{\text{M}kk}}{\rho_{kk}}\varphi'=0,$$

$$\frac{1}{\rho_{ki}}+\frac{1}{\rho_{ik}}\varphi'=0.$$

Determining the value φ' from the second equation and substituting it in the first, we obtain

$$\frac{a_{\text{M}ii}}{\rho_{ii}}\rho_{ki}=\frac{a_{\text{M}kk}}{\rho_{kk}}\rho_{ik}. \tag{19}$$

This gives the relation between the mass transfer coefficients in the expressions for secondary mass transfer vectors appearing in the right sides of (14) and (15).

The equality in question is a mathematical formulation of the Onsager reciprocity principle.

The principle may also be established for energy transfer processes in a composite n-component medium.

The transfer vectors of the i-th and k-th energy components are given by the expressions

$$\mathbf{q}_{\text{э}i}=-a_{\text{э}ii}\operatorname{grad}\varepsilon_{ii}-a_{\text{э}kk}\frac{\varepsilon_{ik}}{\varepsilon_{kk}}\operatorname{grad}\varepsilon_{kk},$$

$$\mathbf{q}_{\text{э}i}=-a_{\text{э}ii}\frac{\varepsilon_{ki}}{\varepsilon_{ii}}\operatorname{grad}\varepsilon_{ii}-a_{\text{э}kk}\operatorname{grad}\varepsilon_{kk}.$$

By examining transfer of the given energy components in the same manner as transfer of the i-th and k-th components of the medium analyzed above, we obtain the following form of the reciprocity principle:

$$\frac{a_{\text{э}ii}}{\varepsilon_{ii}}\varepsilon_{ki}=\frac{a_{\text{э}kk}}{\varepsilon_{kk}}\varepsilon_{ik}. \tag{20}$$

Relation (20) was used by the author in [2].

In conclusion, we point out once again that the reciprocity principle examined is based on the reciprocal relation between the partial mass and energy densities of a moving multi-component medium.

REFERENCES

1. P. K. Konakov, IFZh, [Journal of Engineering Physics], vol. 9, no. 3, 1965.
2. P. K. Konakov, IFZh, no. 6, 1963.

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