

THERMODYNAMICAL THEORY
OF GALVANOMAGNETIC
AND THERMOMAGNETIC PHENOMENA

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AND THERMOMAGNETIC PHENOMENA



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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT
TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS
DR. J. N. BAKHUIZEN VAN DEN BRINK, HOOGLEERAAR
IN DE FACULTEIT DER GODGELEERDHEID, TEGEN DE BE-
DENKINGEN VAN DE FACULTEIT DER WIS- EN NATUUR-
KUNDE TE VERDEDIGEN OP WOENSDAG 10 NOVEMBER 1954,
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DOOR

ROBERTO FIESCHI

GEBOREN TE CREMONA (ITALIË) IN 1928

THE HISTORY OF THE
OF THE
AND

PROMOTOR: PROF. DR S. R. DE GROOT



*alla mamma al papà
ad Anna*

THE UNIVERSITY OF CHICAGO



THE UNIVERSITY OF CHICAGO

1917

VOORWOORD.

Ten einde te voldoen aan de wens van de Faculteit der Wis- en Natuurkunde volgt hier een kort overzicht van mijn academische studie.

In October 1946 begon ik mijn studie in de natuurkunde aan de Universiteit te Pavia (Italië). Ik verkreeg een beurs om aan het « Collegio Universitario Ghislieri » in Pavia te kunnen studeren, welke beurs elk jaar gedurende mijn studie hernieuwd werd. In December 1950 promoveerde ik in de natuurkunde aan genoemde universiteit op een proefschrift, getiteld « Effetti geomagnetici nella radiazione cosmica ».

Tijdens de academische studiejaren 1950-1951 en 1951-1952 was ik als assistent verbonden aan het Instituut voor Theoretische Natuurkunde te Milaan. Als zodanig heb ik daar onder leiding van Prof. Dr P. CALDIROLA en in samenwerking met Dr P. GULMANELLI aan een fenomenologische theorie van de cosmische straling gewerkt. Onder leiding van Prof. Dr F. G. FUMI werkte ik in die tijd ook aan de eigenschappen van verontreinigde alkali-halide-kristallen en op het gebied van tensoren van hoge orde in symmetrische systemen.

Een beurs van de Nederlandse regering en een bijdrage van het Lorentz-fonds stelde mij in staat van October 1952 tot Maart 1954 in Nederland te studeren. In het begin van deze periode heb ik onder leiding van Dr B. R. A. NIJBOER aan radiële distributie-functies in gecomprimeerde gassen gewerkt. Later verrichtte ik onder leiding van Prof. Dr S. R. DE GROOT en Dr P. MAZUR en in samenwerking met J. VLEGER en Ir G. A. KLUITENBERG onderzoekingen op het gebied van de thermodynamica van irreversibele electromagnetische verschijnselen.

PUBLICATIES

Nuovo Cimento, **8**, 508 (1951): Effetto di latitudine sulla distribuzione dei mesoni nell'atmosfera; **9**, 5 (1952): A Phenomenological Theory of Cosmic Radiation in the Atmosphere (met P. CALDIROLA en P. GULMANELLI).

Nuovo Cimento, **10**, 865 (1953): High-order Matter Tensors in Symmetrical Systems (met F. G. FUMI).

Physica, **19**, 545 (1953): On the Radial Distribution Function of a Compressed Gas of Rigid Spheres (met B. R. A. NIJBOER).

Physica, **20**, 67 (1954): Thermodynamical Theory of Galvanomagnetic and Thermomagnetic Phenomena I, Reciprocal Relations in Anisotropic Metals (met S. R. DE GROOT en P. MAZUR); **20**, 245 (1954): II, Reciprocal Relations for Moving Anisotropic Mixtures (met S. R. DE GROOT, P. MAZUR en J. VLEGER); **20**, 259 (1954): III, Explicit Expressions for the Measurable Effects in Isotropic Metals (met S. R. DE GROOT en P. MAZUR).

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SUMMARY

The galvanomagnetic and thermomagnetic phenomena are studied, from the theoretical point of view, using the methods of thermodynamics of irreversible processes. The purpose of this thesis is to consider the problem with the help of an extension of Onsager's theory of reciprocal relations between irreversible processes, given by DE GROOT and MAZUR. This extension allows us to treat vectorial and tensorial phenomena (Chapter I).

We shall give a rigorous derivation of the reciprocal relations for the general case of heat conduction, diffusion (including electrical conduction) and cross-effects, and of viscosity in anisotropic mixtures of charged components in an electromagnetic field. Subsequently the case of an isotropic metal is considered (Chapter II).

The various measurable galvanomagnetic and thermomagnetic effects, and the relations among them, are treated explicitly (Chapter III).

CHAPTER I.

GENERAL THEORY

1. - Thermodynamical Theory of Irreversible Processes.

The thermodynamical theory of irreversible processes^(1,2) is a relatively new branch of science which enables us to treat real processes, from a macroscopic point of view, in a systematic way. The theory is based on two fundamental concepts, the *entropy production* and the *Onsager relations*⁽³⁾, which are briefly introduced in this section.

The entropy production, which is a result of the progress of irreversible processes, can be calculated with the help of the fundamental laws of macroscopic physics: the law of conservation of mass, the equations of motion (momentum law), the first law of thermodynamics (energy conservation law) and the second law of thermodynamics (Gibbs' relation). From the fundamental laws a balance equation for the entropy can be derived:

$$(I.1) \quad \partial s_v / \partial t = - \operatorname{div} (\mathbf{J}_s + s_v \mathbf{v}) + \sigma,$$

which shows that the entropy s_v (per unit volume) changes as a result of an *entropy flow* \mathbf{J}_s and an *entropy production* σ . The divergence of the entropy flow gives the entropy supplied by exchange of energy or matter with the surroundings (it may be positive or negative), while σ arises from the action of irreversible processes inside the system. Calculations show that the entropy production has an expression of the following form:

$$(I.2) \quad \sigma = \sum_i J_i X_i \geq 0,$$

(¹) S. R. DE GROOT: *Thermodynamics of Irreversible Processes* (Amsterdam and New York, 1951).

(²) I. PRIGOGINE: *Étude thermodynamique des phénomènes irréversibles* (Liege, 1947).

(³) L. ONSAGER: *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).

where we have a sum of products of quantities J_i called « fluxes » (e.g., heat flow, diffusion flow, electric current, chemical reaction rate) and corresponding quantities X_i called « forces » or « affinities » (e.g., temperature gradient, gradient of chemical potential, electric field strength, chemical affinity). This expression is a measure of the irreversibility of the processes: it vanishes when the system undergoes only reversible changes, in all other cases it is positive.

In the most general case every flow is caused by contribution of all forces (and inversely). So in the linear approximation the irreversible phenomena can be expressed by the so-called « phenomenological equations », which have the following form:

$$(I.3) \quad J_i = \sum_k L_{ik} X_k.$$

Examples of these laws are, for instance, Fourier's law for the heat conduction, the law which describes the Dufour effect, Fick's law for the diffusion, the thermal diffusion (Soret-effect) law, Ohm's law for the electrical conduction, the laws which describe the thermoelectric effects and the laws which describe the galvanomagnetic and thermomagnetic effects.

The coefficients L_{ik} are called « phenomenological coefficients », and ONSAGER⁽³⁾ has established the following « reciprocal relations » which hold between them:

$$(I.4) \quad L_{ik} = L_{ki},$$

expressing a connection between reciprocal phenomena which arise from mutual interference of simultaneously occurring irreversible processes (*). Many well-known physical relations, which could not be explained by thermostatic considerations, or by considerations on the physical symmetry of the system, are a consequence of the « Onsager relations ». It is allowed to say that the *Onsager relations* are indeed a new and very fundamental law of macroscopic thermodynamics. ONSAGER has shown that they are the macroscopic counterpart of the property of time reversal invariance of the laws which govern the motion of the individual particles forming the system. The demonstration of ONSAGER is based on the general ideas of statistical mechanics, and it will be explained in a modified form in the next section.

2. - De Groot and Mazur's Theory.

2.1. *Casimir's objection and method.* - As CASIMIR⁽⁴⁾ pointed out, ONSAGER's proof is strictly valid only for scalar phenomena. As a matter of fact,

(*) In case there is a magnetic field \mathbf{B} , the phenomenological coefficients can be functions of \mathbf{B} and then the relation (I.4) must be replaced by $L_{ik}(\mathbf{B}) = L_{ki}(-\mathbf{B})$.

(4) H. B. G. CASIMIR: *Rev. Mod. Phys.*, **17**, 343 (1945).

ONSAGER assumes that the irreversible fluxes can be considered time derivatives of thermodynamic state variables. This is correct for scalar processes (such as chemical reactions and relaxation phenomena) but not for vectorial processes, (such as heat conduction, diffusion and electrical conduction), and tensorial processes (such as viscous flow), and therefore an extension of the theory is necessary.

CASIMIR has proposed a method, which he has applied to the case of heat conduction in anisotropic crystals without magnetic field: he reformulates the problem under investigation in such a way that it is possible to apply the original Onsager formalism. To achieve this aim it is necessary to introduce appropriate auxiliary phenomenological equations containing an infinite number of coefficients, which are only indirectly related to the ordinary macroscopic laws and coefficients. MAZUR and DE GROOT ⁽⁵⁾ have also considered systems with magnetic fields, and derived reciprocal relations for the heat and electrical conduction tensors.

2.2. *Basis of the method of De Groot and Mazur.* - To solve the problem of finding reciprocal relations for vectorial and tensorial processes, DE GROOT and MAZUR ⁽⁶⁾ have developed a different method, which is in a certain sense the opposite of the first: now the phenomenological problem is not rewritten in a form appropriate for the application of the original Onsager theory, but the formalism is generalized in such a way that it can be applied also for fluxes which describe vectorial and tensorial irreversible phenomena, or, in other words, for fluxes which are not necessarily time derivatives of state variables. In this theory the ordinary macroscopic laws can be used as phenomenological equations, and thus the complications inherent in the approach of the first method are avoided. With the help of a generalization of the fluctuation theory, (cf. also ^(6-bis)), reciprocal relations for vectorial and tensorial processes can be derived directly from the property of microscopic reversibility.

2.3. *Fluctuation theory.* - We consider an energetically insulated system. The thermodynamic state of the system is described by variables A_1, A_2, \dots, A_m , which are even functions of the particle velocities, and variables $B_{m+1}, B_{m+2}, \dots, B_n$, which are odd functions of the particle velocities (the B -type variables, or their divergences, may be time derivatives of A -type variables: cf. also ⁽⁴⁾). All variables are continuous functions of space and time coordinates. For convenience the system will be divided into a number of cells of volume V^u , in which the thermodynamic variables may be considered as uniform (here

⁽⁵⁾ P. MAZUR and S. R. DE GROOT: *Physica*, **19**, 961 (1953).

⁽⁶⁾ S. R. DE GROOT and P. MAZUR: *Phys. Rev.*, **94**, 218 (1954); *Supplemento al Nuovo Cimento*, **12**, 5 (1954).

^(6-bis) J. VLEIGER and S. R. DE GROOT: *Physica*, **20**, 372 (1954).

μ numbers the cells). The deviations of the state variables from their equilibrium values are denoted by

$$(I.5) \quad \alpha_i^\mu = A_i^\mu - (A_i^\mu)_{\text{equ}}, \quad (i = 1, 2, \dots, m)$$

$$(I.6) \quad \beta_k^\mu = B_k^\mu - (B_k^\mu)_{\text{equ}}, \quad (k = m+1, m+2, \dots, n)$$

Since the entropy has a maximum in the equilibrium state, the deviation of the entropy of the system from its equilibrium value is given, as a first approximation, by the quadratic form

$$(I.7) \quad \Delta S = -\frac{1}{2} \sum_{\mu, \nu} V^\mu V^\nu \left(\sum_{i,j} g_{ij}^{\mu\nu} \alpha_i^\mu \alpha_j^\nu + \sum_{k,l} h_{kl}^{\mu\nu} \beta_k^\mu \beta_l^\nu \right),$$

where $g_{ij}^{\mu\nu}$ and $h_{kl}^{\mu\nu}$ are positive definite forms.

Since the entropy is an even function of the particle velocities no cross-terms between α - and β -variables appear in the expression (I.7). The probability distribution for the α_i^μ and β_k^μ is expressed by

$$(I.8) \quad P \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu = \frac{\exp[\Delta S/k] \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu}{\int \dots \int \exp[\Delta S/k] \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu},$$

where k is Boltzmann's constant.

The following linear combinations of parameters are introduced:

$$(I.9) \quad X_i^\mu = (V^\mu)^{-1} \partial \Delta S / \partial \alpha_i^\mu = - \sum_\nu V^\nu \sum_j g_{ij}^{\mu\nu} \alpha_j^\nu,$$

$$(I.10) \quad Y_k^\mu = (V^\mu)^{-1} \partial \Delta S / \partial \beta_k^\mu = - \sum_\nu V^\nu \sum_l h_{kl}^{\mu\nu} \beta_l^\nu,$$

which will be designed as conjugate variables.

The following averages can easily be found with the help of (I.8)-(I.10):

$$(I.11) \quad \overline{\alpha_i^\mu(t) X_j^\nu(t)} = -k \delta_{ij} \delta_{\mu\nu} / V^\mu,$$

$$(I.12) \quad \overline{\beta_k^\mu(t) Y_l^\nu(t)} = -k \delta_{kl} \delta_{\mu\nu} / V^\mu,$$

where δ is the Kronecker symbol.

Here and in the following, according to the fundamental notions of statistical mechanics, the average may be interpreted either as an average over a microcanonical ensemble of systems, or as a time average for one single system.

Average values of products of α - and β -type variables always vanish.

Passing to the limit of continuous variables, the indices μ and ν of (I.11) and (I.12), which indicate the cells, can be replaced by \mathbf{r} and \mathbf{r}' , which denote space coordinates, whereas the last two factors of (I.11) and (I.12) combine

into a Heaviside-Dirac δ function. Consequently (I.11) and (I.12) become

$$(I.13) \quad \overline{\alpha_i(\mathbf{r}, t)\chi_j(\mathbf{r}', t)} = -k \delta_{ij} \delta(\mathbf{r} - \mathbf{r}'),$$

$$(I.14) \quad \overline{\beta_k(\mathbf{r}, t)y_l(\mathbf{r}', t)} = -k \delta_{kl} \delta(\mathbf{r} - \mathbf{r}').$$

From (I.13) and (I.14) one can immediately derive the formulae

$$(I.15) \quad \overline{\alpha_i(\mathbf{r}, t)\Omega(\mathbf{r}')\chi_j(\mathbf{r}', t)} = -k \delta_{ij} \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'),$$

$$(I.16) \quad \overline{\beta_k(\mathbf{r}, t)\Omega(\mathbf{r}')y_l(\mathbf{r}', t)} = -k \delta_{kl} \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'),$$

where $\Omega(\mathbf{r})$ is a differential operator of the general form

$$(I.17) \quad \Omega(\mathbf{r}) = \sum_{p,q,s} a_{p,q,s}(\mathbf{r}) \partial^{p+q+s} / \partial x_1^p \partial x_2^q \partial x_3^s.$$

The coefficients $a_{p,q,s}$ are independent of the state variables $\beta_k(\mathbf{r}, t)$ and $\alpha_i(\mathbf{r}, t)$; the Cartesian coordinates are denoted by x_1 , x_2 and x_3 .

The formulae (I.15) and (I.16) serve as an extremely useful basis for the straightforward derivation of the reciprocal relations among phenomenological coefficients.

Remark. It may be noted that with (I.9) and (I.10) the time derivative of (I.7) (entropy production per unit time) can be written as

$$(I.18) \quad \Delta \dot{S} = \sum_{\mu} V^{\mu} (\sum_i \dot{\alpha}_i^{\mu} \chi_i^{\mu} + \sum_k \dot{\beta}_k^{\mu} y_k^{\mu}),$$

or

$$(I.19) \quad \Delta \dot{S} = \int \{ \sum_i \dot{\alpha}_i(\mathbf{r}) \chi_i(\mathbf{r}) + \sum_k \dot{\beta}_k(\mathbf{r}) y_k(\mathbf{r}) \} d\mathbf{r},$$

in the limit of infinitely small cells. One sees that state variables and conjugate variables can be identified either from the expression for the deviation of the entropy, or from the expression for the entropy production (I.19).

2.4. *Microscopic reversibility.* - The fact that, on the average, the future behaviour of a system is identical with its past behaviour, will now be expressed with the help of correlation functions. Since a magnetic field \mathbf{B} is present, it is necessary to reverse its direction in every point in order to have the particles retracing their paths. Minus sign arises when an α -type variable is combined with a β -type variable (^{4,1}):

$$(I.20) \quad \overline{\alpha_i(\mathbf{r}, t)\alpha_j(\mathbf{r}', t+\tau)} \{\mathbf{B}, \mathbf{B}'\} = \overline{\alpha_j(\mathbf{r}', t)\alpha_i(\mathbf{r}, t+\tau)} \{-\mathbf{B}, -\mathbf{B}'\},$$

$$(I.21) \quad \overline{\alpha_i(\mathbf{r}, t)\beta_l(\mathbf{r}', t+\tau)} \{\mathbf{B}, \mathbf{B}'\} = -\overline{\beta_l(\mathbf{r}', t)\alpha_i(\mathbf{r}, t+\tau)} \{-\mathbf{B}, -\mathbf{B}'\},$$

$$(I.22) \quad \overline{\beta_i(\mathbf{r}, t)\beta_m(\mathbf{r}', t+\tau)} \{\mathbf{B}, \mathbf{B}'\} = \overline{\beta_m(\mathbf{r}', t)\beta_i(\mathbf{r}, t+\tau)} \{-\mathbf{B}, -\mathbf{B}'\}.$$

From these three relations it follows that

$$(I.23) \quad \overline{\alpha_i(\mathbf{r}, t)(\partial/\partial t)\alpha_j(\mathbf{r}', t) \{ \mathbf{B}, \mathbf{B}' \}} = \overline{\alpha_j(\mathbf{r}', t)(\partial/\partial t)\alpha_i(\mathbf{r}, t) \{ -\mathbf{B}, -\mathbf{B}' \}},$$

$$(I.24) \quad \overline{\alpha_i(\mathbf{r}, t)(\partial/\partial t)\beta_l(\mathbf{r}', t) \{ \mathbf{B}, \mathbf{B}' \}} = -\overline{\beta_l(\mathbf{r}', t)(\partial/\partial t)\alpha_i(\mathbf{r}, t) \{ -\mathbf{B}, -\mathbf{B}' \}},$$

$$(I.25) \quad \overline{\beta_l(\mathbf{r}, t)(\partial/\partial t)\beta_m(\mathbf{r}', t) \{ \mathbf{B}, \mathbf{B}' \}} = \overline{\beta_m(\mathbf{r}', t)(\partial/\partial t)\beta_l(\mathbf{r}, t) \{ -\mathbf{B}, -\mathbf{B}' \}}.$$

\mathbf{B} and \mathbf{B}' indicate the magnetic field strengths at the positions \mathbf{r} and \mathbf{r}' where the averages are performed. The time derivative in the last three relations should be interpreted on a microscopic scale as the average decay of the fluctuations, which is described by difference quotients (^{4,1}); however, for all practical macroscopic purposes this quotient can be considered as a real derivative.

2.5. *Regression of fluctuations.* - In order to find the reciprocal relations between the phenomenological coefficients, it is necessary to express the time derivatives of the state variables α_i and β_k as functions of the other state quantities χ_i and y_k or of their derivatives with respect to space coordinates. (As a matter of fact we shall write instead of the state variables, their deviations from the equilibrium value). That can be achieved with the use of the conservation laws and the entropy balance equations, and one obtains expressions of the kind

$$(I.26) \quad \partial\alpha_i/\partial t = \sum_k \Omega_{ik}^{\alpha\alpha} \chi_k + \sum_h \Omega_{ih}^{\alpha\beta} y_h,$$

$$(I.27) \quad \partial\beta_i/\partial t = \sum_k \Omega_{ik}^{\beta\alpha} \chi_k + \sum_h \Omega_{ih}^{\beta\beta} y_h.$$

The operators Ω_{ik} and Ω_{ih} turn out to be like the following: $\mathbf{L}_{ik} \cdot$, $\mathbf{L}_{ik} \cdot \text{grad}$, $\text{div}(\mathbf{L}_{ik} \cdot)$, $\text{div}(\mathbf{L}_{ik} \cdot \text{grad})$, etc. The subscripts indicate here the fluxes and the forces, not the Cartesian components).

2.6 *Derivation of the Onsager relations.* - With the preceding results, and the usual assumption that the average decay of fluctuations follows the phenomenological macroscopic laws, (which is true for linear phenomena, so that we can take for the average decay of fluctuations, which appears in formulae (I.22)-(I.23), the expressions (I.26) and (I.27)), the derivation of Onsager relations is straightforward. Introducing (I.26) and (I.27) into (I.23)-(I.25) one has

$$(I.28) \quad \overline{\alpha_i(\mathbf{r}) \left\{ \sum_k \Omega_{jk}^{\alpha\alpha}(\mathbf{r}', \mathbf{B}') \chi_k(\mathbf{r}') + \sum_h \Omega_{jh}^{\alpha\beta}(\mathbf{r}', \mathbf{B}') y_h(\mathbf{r}') \right\} \{ \mathbf{B}, \mathbf{B}' \}} = \\ = \overline{\alpha_j(\mathbf{r}') \left\{ \sum_k \Omega_{ik}^{\alpha\alpha}(\mathbf{r}, -\mathbf{B}) \chi_k(\mathbf{r}) + \sum_h \Omega_{ih}^{\alpha\beta}(\mathbf{r}, -\mathbf{B}) y_h(\mathbf{r}) \right\} \{ -\mathbf{B}, -\mathbf{B}' \}},$$

$$(I.29) \quad \overline{\alpha_i(\mathbf{r}) \left\{ \sum_k \Omega_{ik}^{\beta\alpha}(\mathbf{r}', \mathbf{B}') \chi_k(\mathbf{r}') + \sum_h \Omega_{ih}^{\beta\beta}(\mathbf{r}', \mathbf{B}') y_h(\mathbf{r}') \right\}} \{ \mathbf{B}, \mathbf{B}' \} = \\ = - \overline{\beta_i(\mathbf{r}') \left\{ \sum_k \Omega_{ik}^{\alpha\alpha}(\mathbf{r}, -\mathbf{B}) \chi_k(\mathbf{r}) + \sum_h \Omega_{ih}^{\alpha\beta}(\mathbf{r}, -\mathbf{B}) y_h(\mathbf{r}) \right\}} \{ -\mathbf{B}, -\mathbf{B}' \},$$

$$(I.30) \quad \overline{\beta_i(\mathbf{r}) \left\{ \sum_k \Omega_{mk}^{\beta\alpha}(\mathbf{r}', \mathbf{B}') \chi_k(\mathbf{r}') + \sum_h \Omega_{mh}^{\beta\beta}(\mathbf{r}', \mathbf{B}') y_h(\mathbf{r}') \right\}} \{ \mathbf{B}, \mathbf{B}' \} = \\ = \overline{\beta_m(\mathbf{r}') \left\{ \sum_k \Omega_{ik}^{\beta\alpha}(\mathbf{r}, -\mathbf{B}) \chi_k(\mathbf{r}) + \sum_h \Omega_{ih}^{\beta\beta}(\mathbf{r}, -\mathbf{B}) y_h(\mathbf{r}) \right\}} \{ -\mathbf{B}, -\mathbf{B}' \}.$$

According to (I.15) and (I.16) these relations lead to

$$(I.31) \quad -k \delta_{ik} \Omega_{jk}^{\alpha\alpha}(\mathbf{r}', \mathbf{B}') \delta(\mathbf{r} - \mathbf{r}') = -k \delta_{jk} \Omega_{ik}^{\alpha\alpha}(\mathbf{r}, -\mathbf{B}) \delta(\mathbf{r} - \mathbf{r}'),$$

$$(I.32) \quad -k \delta_{ik} \Omega_{ik}^{\beta\alpha}(\mathbf{r}', \mathbf{B}') \delta(\mathbf{r} - \mathbf{r}') = +k \delta_{ih} \Omega_{ih}^{\alpha\beta}(\mathbf{r}, -\mathbf{B}) \delta(\mathbf{r} - \mathbf{r}'),$$

$$(I.33) \quad -k \delta_{ih} \Omega_{mh}^{\beta\beta}(\mathbf{r}', \mathbf{B}') \delta(\mathbf{r} - \mathbf{r}') = -k \delta_{mh} \Omega_{ih}^{\beta\beta}(\mathbf{r}, -\mathbf{B}) \delta(\mathbf{r} - \mathbf{r}').$$

Elimination of the Kronecker δ 's and the δ -functions gives now the relations for the phenomenological coefficients, which are contained into the operators Ω , either simply

$$(I.34) \quad L_{ik}(\mathbf{B}) = L_{ki}(-\mathbf{B}),$$

or in a form containing differential operators, e.g.

$$(I.35) \quad \text{Div } L_{ik}(\mathbf{B}) = \text{Div } L_{ki}(-\mathbf{B}),$$

according to the actual expression of Ω for the various cases.

Remark. Onsager's demonstration was valid for the case $J_i \equiv \partial \alpha_i / \partial t$ and $X_i \equiv X_i$. Reciprocal relations are then immediately obtained: since $\Omega_{ik} \equiv L_{ik}$, and from (I.3), (I.23) and (I.15), follows $L_{ik} = L_{ki}$.

CHAPTER II.

DERIVATION OF THE RECIPROCAL RELATIONS

1. - Introduction.

In this chapter the general theory outlined above ⁽⁶⁾ is applied to the case of mixtures of n charged components in an electromagnetic field ⁽⁷⁾. In such a general case the irreversible phenomena of heat conduction, diffusion (including electric conduction) and cross-effects, and of viscous flow, occur.

First the macroscopic phenomenological theory of the case mentioned is developed: in § 2 the entropy production in local form is calculated from the fundamental laws; in § 3 the phenomenological equations are written down.

Subsequently the fluctuation theory is developed and the reciprocal relations for the phenomenological coefficients are obtained (§§ 4-10). In § 4 we derive an expression for the total entropy production in an energetically insulated system in terms of fluctuations of independent thermodynamic state variables; in § 5 fluctuation averages are calculated, and in the next section (§ 6) the microscopic time reversibility property is expressed by means of correlation functions. From the phenomenological equations, the conservation laws and the entropy balance, we derive in § 7 the expression for the regression of fluctuations of the state variables. The equation for the decay of the vector potential requires special attention. In §§ 8, 9 and 10 the reciprocal relations for the phenomenological coefficients are derived. It is found that one gets physical results from time reversibility relations, in which both even and odd variables occur ⁽⁴⁾.

The last part of the chapter (§§ 11 and 12) shows how the description of simpler phenomena can be obtained by specializing the results of the more general case. In particular the equations which describe the galvanomagnetic and thermomagnetic phenomena are considered.

(7) R. FIESCHI, S. R. DE GROOT, P. MAZUR and J. VLIJGER: *Physica*, 20, 67 (1954).

2. - Entropy Production in Local Form.

Let us consider a mixture of n charged non-reacting components in an electromagnetic field and subject to external conservative (non-electrical) forces. Magnetization and polarization are neglected. The entropy production can be calculated from the fundamental laws of macroscopic physics^(1,8) (cf. chap. I, § 2).

The law of conservation of mass. - As chemical reactions are not taken into consideration, this law can be written as follows for the component k :

$$(II.1) \quad \rho \, dc_k/dt = - \operatorname{div} \mathbf{J}_k, \quad (k = 1, 2, \dots, n)$$

where ρ is the total density, c_k the mass fraction of component k ($\sum_{k=1}^n c_k = 1$) and $\mathbf{J}_k = \rho_k(\mathbf{v}_k - \mathbf{v})$ the diffusion flow of k with respect to the centre of gravity motion ($\rho_k = c_k \rho$ is density of component k , \mathbf{v}_k is velocity of k and \mathbf{v} is barycentric velocity). From the definition of \mathbf{J}_k it follows that $\sum_{k=1}^n \mathbf{J}_k = 0$. Furthermore we have

$$(II.2) \quad \rho \, dv/dt = \operatorname{div} \mathbf{v}.$$

Here $v = \rho^{-1}$ is the specific volume. In (II.1) and (II.2) d/dt is the substantial time derivative with respect to the centre of mass motion:

$$(II.3) \quad d/dt = \partial/\partial t + \mathbf{v} \cdot \operatorname{grad}.$$

With (II.3) the formulae (II.1) and (II.2) can also be written as

$$(II.4) \quad \partial \rho_k / \partial t = - \operatorname{div} \rho_k \mathbf{v} - \operatorname{div} \mathbf{J}_k,$$

$$(II.5) \quad \partial \rho / \partial t = - \operatorname{div} \rho \mathbf{v}.$$

The momentum law.

$$(II.6) \quad \rho \, d\mathbf{v}/dt = - \operatorname{Div} \mathbf{P}^t + \sum_{k=1}^n \rho_k \mathbf{F}_k^{(L)} + \sum_{k=1}^n \rho_k \mathbf{F}_k.$$

⁽⁸⁾ P. MAZUR and I. PRIGOGINE: *Acad. Roy. Belg., Classe des Sciences, Mém.*, 28, fasc. 1 (1953).

$\mathbf{F}_k^{(L)}$ is the Lorentz electromagnetic force per unit mass, acting on component k :

$$(II.7) \quad \mathbf{F}_k^{(L)} = e_k \{ \mathbf{E} + c^{-1}(\mathbf{v}_k \wedge \mathbf{B}) \}, \quad (k = 1, 2, \dots, n)$$

where \mathbf{E} is the electric field strength, \mathbf{B} the magnetic induction, e_k the charge per unit mass of component k . \mathbf{F}_k is an external (non-electrical) conservative force, also per unit mass of k :

$$(II.8) \quad \mathbf{F}_k = -\text{grad } w_k; \quad \text{with } \partial w_k / \partial t = 0, \quad (k = 1, 2, \dots, n)$$

where w_k is the potential energy per unit mass of k . \mathbf{P} is the pressure tensor

$$(II.9) \quad \mathbf{P} = p\delta + \mathbf{\Pi},$$

with δ the unit tensor, p the hydrostatic pressure and $\mathbf{\Pi}$ the viscous pressure tensor. The sign \dagger means transposing of the Cartesian components of a tensor.

Introducing the total charge density

$$(II.10) \quad \rho e = \sum_{k=1}^n \rho_k e_k,$$

and the conduction current

$$(II.11) \quad \mathbf{i} = \sum_{k=1}^n e_k \mathbf{J}_k,$$

formula (II.6) can be written as

$$(II.12) \quad \rho \, d\mathbf{v}/dt = -\text{Div } \mathbf{P}^\dagger + \rho e \{ \mathbf{E} + c^{-1}(\mathbf{v} \wedge \mathbf{B}) \} + c^{-1}(\mathbf{i} \wedge \mathbf{B}) + \sum_{k=1}^n \rho_k \mathbf{F}_k.$$

Scalar multiplication of (II.12) with \mathbf{v} gives the balance of the kinetic energy per unit of mass $l = \frac{1}{2}\mathbf{v}^2$:

$$(II.13) \quad \rho \, dl/dt = -\mathbf{v} \cdot \text{Div } \mathbf{P}^\dagger + \rho e \mathbf{v} \cdot \mathbf{E} - c^{-1} \mathbf{i} \cdot (\mathbf{v} \wedge \mathbf{B}) + \sum_{k=1}^n \rho_k \mathbf{v} \cdot \mathbf{F}_k.$$

Using (II.3), (II.5) and (II.8), we can write (II.12) alternatively as

$$(II.14) \quad \begin{aligned} \partial \mathbf{g} / \partial t = & -\text{Div} (\mathbf{g} \mathbf{v} + \mathbf{P}^\dagger) - \rho e \{ \text{grad } \varphi + c^{-1}(\partial \mathbf{A} / \partial t - \mathbf{v} \wedge \mathbf{B}) \} + \\ & + c^{-1}(\mathbf{i} \wedge \mathbf{B}) - \sum_{k=1}^n \rho_k \text{grad } w_k, \end{aligned}$$

where $\mathbf{g} = \rho \mathbf{v}$ is the momentum density; furthermore use has been made of

$$(II.15) \quad \mathbf{E} = -\text{grad } \varphi - c^{-1} \partial \mathbf{A} / \partial t,$$

where φ is the scalar potential and \mathbf{A} the vector potential.

Energy law. - The energy of the electromagnetic field per unit of volume is

$$(II.16) \quad f_v = \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2).$$

The balance equation of f_v is Poynting's law

$$(II.17) \quad \partial f_v / \partial t = -\operatorname{div} c(\mathbf{E} \wedge \mathbf{B}) - \rho_e \mathbf{v} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E},$$

where $c(\mathbf{E} \wedge \mathbf{B})$ is the Poynting vector. With (II.2) and (II.3) formula (II.17) can also be written as

$$(II.18) \quad \rho \, df/dt = -\operatorname{div} \{c(\mathbf{E} \wedge \mathbf{B}) - f_v \mathbf{v}\} - \rho_e \mathbf{v} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E},$$

where $f = f_v$, v is the electromagnetic energy per unit mass.

For the potential energy $w = \sum_{k=1}^n c_k w_k$ per unit mass, we have

$$(II.19) \quad dw/dt = -\operatorname{div} \left(\sum_{k=1}^n w_k \mathbf{J}_k \right) - \sum_{k=1}^n \rho_k \mathbf{v}_k \cdot \mathbf{F}_k,$$

where (II.1), (II.3) and (II.8) have been applied.

The energy equation can be written as

$$(II.20) \quad \rho \, de/dt = -\operatorname{div} \mathbf{J}_e,$$

where e is the total energy per unit mass and \mathbf{J}_e the energy flow. These are given by

$$(II.21) \quad e = u + l + f + w,$$

$$(II.22) \quad \mathbf{J}_e = \mathbf{J}_q + \mathbf{v} \cdot \mathbf{P} + c(\mathbf{E} \wedge \mathbf{B}) - f_v \mathbf{v} + \sum_{k=1}^n w_k \mathbf{J}_k,$$

with u the internal energy per unit of mass. Equation (II.22) defines the heat flow \mathbf{J}_q . [The balance equation of $e_v = e \rho$ can be written as

$$(II.23) \quad \partial e_v / \partial t = -\operatorname{div} \mathbf{J}_{e, \text{tot}} = -\operatorname{div} (\mathbf{J}_e + e_v \mathbf{v}),$$

with

$$(II.24) \quad \mathbf{J}_{e, \text{tot}} = u_v \mathbf{v} + l_v \mathbf{v} + w_v \mathbf{v} + \mathbf{J}_q + \mathbf{v} \cdot \mathbf{P} + c(\mathbf{E} \wedge \mathbf{B}) + \sum_{k=1}^n w_k \mathbf{J}_k,$$

which follows from (II.22) and $e_v = u_v + l_v + f_v + w_v$ (the index v means per unit volume). In the formula (II.24) the electromagnetic (« anti »)-convection term $-f_v \mathbf{v}$ has disappeared, in place of which one has the ordinary convection terms $u_v \mathbf{v}$, $l_v \mathbf{v}$ and $w_v \mathbf{v}$].

The first law of thermodynamics (internal energy balance) is found by deducting (II.13), (II. 18) and (II.19) from (II.20) (with (II.21) and (II.22)):

$$(II.25) \quad \rho \, du/dt = -\operatorname{div} \mathbf{J}_q + \mathbf{i} \cdot \{ \mathbf{E} + c^{-1}(\mathbf{v} \wedge \mathbf{B}) \} + \sum_{k=1}^n \mathbf{F}_k \cdot \mathbf{J}_k - \mathbf{P} : \operatorname{Grad} \mathbf{v}.$$

Gibb's law.

$$(II.26) \quad T \, ds/dt = du/dt + p \, dv/dt - \sum_{k=1}^n \mu_k \, dc_k/dt,$$

where T is the temperature, s the entropy per unit mass and μ_k the chemical potential per unit mass.

Entropy balance. - Introducing (II.1), (II.2) and (II.25) and using also (II.9) and (II.11), equation (II.26) can be written as a balance equation,

$$(II.27) \quad \rho \, ds/dt = -\operatorname{div} \mathbf{J}_s + \sigma,$$

where \mathbf{J}_s is the entropy flow

$$(II.28) \quad \mathbf{J}_s = (\mathbf{J}_q - \sum_{k=1}^n \mu_k \mathbf{J}_k) / T,$$

and where the entropy production σ follows from

$$(II.29) \quad T\sigma = -\mathbf{J}_q \cdot (\operatorname{grad} T) / T + \sum_{k=1}^n \mathbf{J}_k \cdot [e_k \{ \mathbf{E} + c^{-1}(\mathbf{v} \wedge \mathbf{B}) \} + \mathbf{F}_k - \\ - T \operatorname{grad} (\mu_k / T)] - \mathbf{\Pi} : \operatorname{Grad} \mathbf{v} \geq 0.$$

The three terms on the right-hand side of (II.29) are the results of entropy production due to heat conduction, diffusion and viscous flow respectively.

Hereunder we shall use another form of $T\sigma$, which follows from (II.8), (II, 15) and (II.28):

$$(II.30) \quad T\sigma = -\mathbf{J}_s \cdot \operatorname{grad} T - \sum_{k=1}^n \mathbf{J}_k \cdot \{ \operatorname{grad} \tilde{\mu}_k + e_k c^{-1} (\partial \mathbf{A} / \partial t - \mathbf{v} \wedge \mathbf{B}) \} - \\ - \mathbf{\Pi} : \operatorname{Grad} \mathbf{v} > 0,$$

where the quantity

$$(II.31) \quad \tilde{\mu}_k = \mu_k + e_k \varphi + w_k \quad (k = 1, 2, \dots, n)$$

has been introduced.

Finally from (II.3), (II.5) and (II.27) one finds

$$(II.32) \quad \partial s_v / \partial t = -\operatorname{div} (s_v \mathbf{v} + \mathbf{J}_s) + \sigma,$$

where $s_v = \rho s$ is the entropy per unit of volume.

Remark. From (II.30) (or (II.29)) one can see that, when the barycentric velocity vanishes, the magnetic part of the Lorentz force does not give any explicit contribution to the entropy production. It can however be shown (in an analogous way as it has been done by HOOYMAN and others⁽⁹⁾ for the case of the Coriolis forces) that an implicit dependence may exist.

3. - Phenomenological Equations.

In (II.30) $T\sigma$ is seen to be a sum of the products of two sets of variables, viz. the first set \mathbf{J}_s , \mathbf{J}_k and Π , which are called « fluxes », and the second set $-\operatorname{grad} T$, $-\{\operatorname{grad} \tilde{\mu}_k + e_k c^{-1}(\partial A / \partial t - \mathbf{v} \wedge \mathbf{B})\}$ and $-\operatorname{Grad} \mathbf{v}$, which are called « forces » or « affinities » (*) (cf. (I.2)). With these fluxes and forces we can establish the « phenomenological equations » as the linear relations (cf. (I.3))

$$(II.33) \quad \mathbf{J}_s = -\mathbf{L}_{ss} \cdot \operatorname{grad} T - \sum_{l=1}^n \mathbf{L}_{sl} \cdot \{\operatorname{grad} \tilde{\mu}_l + e_l c^{-1}(\partial A / \partial t - \mathbf{v} \wedge \mathbf{B})\},$$

$$(II.34) \quad \mathbf{J}_k = -\mathbf{L}_{ks} \cdot \operatorname{grad} T - \sum_{l=1}^n \mathbf{L}_{kl} \cdot \{\operatorname{grad} \tilde{\mu}_l + e_l c^{-1}(\partial A / \partial t - \mathbf{v} \wedge \mathbf{B})\},$$

($k = 1, 2, \dots, n$)

$$(II.35) \quad \Pi_{ij} = -\sum_{m,n=1}^3 L_{ij, mn} (\operatorname{Grad} \mathbf{v})_{mn}, \quad (i, j = 1, 2, 3)$$

(k and l denote chemical components, i , j , m and n Cartesian components). In these formulae cross-effects between fluxes and forces of different tensorial character are not taken into consideration, although such effects might exist

⁽⁹⁾ G. J. HOYMAN, H. HOLTAN JR., P. MAZUR and S. R. DE GROOT: *Physica*, **19**, 1095 (1953).

(*) The parameter T which multiplies σ can be included in the phenomenological coefficients, hence it is not taken into account in the expression of the forces.

in anisotropic media. The present formalism could of course be easily extended to such a case. (In isotropic media these cross-effects do not exist, according to the so-called Curie-principle).

The tensors \mathbf{L}_{sl} , \mathbf{L}_{ks} and \mathbf{L}_{kl} ($k, l=1, 2, \dots, n$) are not independent, because the relation

$$(II.36) \quad \sum_{k=1}^n \mathbf{J}_k = 0$$

holds. Equations containing independent coefficients, however, are easily obtained when the dependent flow \mathbf{J}_n is eliminated from the expression of the entropy production. From (II.30) and (II.36) one has

$$(II.37) \quad T\sigma = -\mathbf{J}_s \cdot \text{grad } T - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \{ \text{grad } (\tilde{\mu}_k - \tilde{\mu}_n) + (e_k - e_n) e^{-1} (\partial \mathcal{A} / \partial t - \mathbf{v} \wedge \mathbf{B}) \} - \mathbf{\Pi} : \text{Grad } \mathbf{v},$$

hence the phenomenological equations

$$(II.38) \quad \mathbf{J}_s = -\mathbf{L}_{ss} \cdot \text{grad } T - \sum_{l=1}^{n-1} \mathbf{L}_{sl} \cdot \{ \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n) - (e_l - e_n) e^{-1} (\partial \mathcal{A} / \partial t - \mathbf{v} \wedge \mathbf{B}) \},$$

$$(II.39) \quad \mathbf{J}_k = -\mathbf{L}_{ks} \cdot \text{grad } T - \sum_{l=1}^{n-1} \mathbf{L}_{kl} \cdot \{ \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n) - (e_l - e_n) e^{-1} (\partial \mathcal{A} / \partial t - \mathbf{v} \wedge \mathbf{B}) \},$$

$$(k=1, 2, \dots, n-1)$$

By using (II.36) and by comparing the new sets of equations with equations (II.33) and (II.34) one can easily prove that the new coefficients coincide with those coefficients of the first set, which have the same subscripts, and it can be shown that the following relations exist:

$$(II.40) \quad \sum_{k=1}^n \mathbf{L}_{ks} = 0, \quad \sum_{k=1}^n \mathbf{L}_{kl} = 0, \quad \sum_{k=1}^n \mathbf{L}_{sk} = 0, \quad \sum_{k=1}^n \mathbf{L}_{lk} = 0. \quad (l=1, 2, \dots, n)$$

We now consider the phenomenological equations (II.35). We shall take the case usually considered of a symmetric tensor $\mathbf{\Pi}$. Then in (II.30) only the symmetric part of the tensor $\text{Grad } \mathbf{v}$ is left. Therefore, instead of (II.35), we have

$$(II.41) \quad \Pi_{(ij)} = - \sum_{m,n=1}^3 L_{(ij),(mn)} (\text{Grad } \mathbf{v})_{(mn)},$$

where the notations (ij) and (mn) indicate the symmetrical character in the indices between brackets. Consequently we are left with 36 phenomenological coefficients $L_{(ij),(mn)}$ instead of 81 coefficients $L_{ij,mn}$ from (II.35).

4. - Entropy Production in Terms of Fluctuations.

In order to apply the fluctuation theory one should know the fluctuation of the entropy (I.7) of the whole energetically insulated system, in terms of the fluctuations of the parameters (I.5), (I.6) which determine the thermodynamical state of the system, and of the variables conjugated to these parameters (I.9), (I.10). However one can see that state variables and conjugate quantities can as well be found from the expression (I.19) for the entropy production per unit time, which is generally used instead of the fluctuation of the entropy (*).

The change of the entropy per unit time dS/dt of the whole adiabatically insulated system in terms of fluctuations will be found^(10,11) by integrating (II.30) over the volume of the system, using the balance equations for mass, momentum and entropy and applying the boundary conditions for the insulation of the system.

Integration of (II.30) gives

$$(II.42) \quad \int_V T \sigma dV = - \int_V \left\{ \mathbf{J}_s \cdot \text{grad } \Delta T + \sum_{k=1}^n \mathbf{J}_k \cdot \text{grad } \Delta \tilde{\mu}_k + \mathbf{\Pi} : \text{Grad } \Delta \mathbf{v} + \right. \\ \left. + \Delta \mathbf{i} \cdot e^{-1} \partial \Delta \mathbf{A} / \partial t - e^{-1} \Delta \mathbf{i} \cdot (\Delta \mathbf{v} \wedge \mathbf{B}) \right\} dV,$$

were we have written, instead of the variables T , $\tilde{\mu}_k$, \mathbf{A} , \mathbf{v} and \mathbf{i} their fluctuations around their equilibrium values (+) and where (II.11) has been used. Partial integration of the first three terms on the right hand side of (II.42),

(*) The use of either expression is of course correct when no relation exists between the time derivative of a state variable and other state variables. When this is not the case, however, one can have, in general, different results from the two expressions. In the present case it can be seen from (II.4) and (II.11) that relations of the mentioned kind exist. Nevertheless, since these are relations between the time derivative of a variable which is an even function of the particle velocities (α -type variable) and variables which are odd functions of the particle velocities (β -type variables), no possibility of confusion may arise: this results from the fact that entropy is an even function of the particle velocities, and is expressed by quadratic terms containing either α -type variables or β -type variables separately ((I.7)).

⁽¹⁰⁾ P. MAZUR and S. R. DE GROOT: *Phys. Rev.*, **94**, 224 (1954).

⁽¹¹⁾ R. FIESCHI, S. R. DE GROOT and P. MAZUR: *Physica*, **20**, 67 (1954).

(+) We have put $\Delta T = T - T_0$, $\Delta \tilde{\mu}_k = \tilde{\mu}_k - \tilde{\mu}_{0,k}$, $\Delta \mathbf{A} = \mathbf{A} - \mathbf{A}_0$, $\Delta \mathbf{v} = \mathbf{v} - \mathbf{v}_0$ and $\Delta \mathbf{i} = \mathbf{i} - \mathbf{i}_0$, (T_0 , $\tilde{\mu}_{0,k}$, \mathbf{A}_0 , \mathbf{v}_0 and \mathbf{i}_0 being the equilibrium values), and have applied the equilibrium conditions, which require the constancy in time of all parameters, the uniformity of T_0 and $\tilde{\mu}_{0,k}$, and the vanishing of \mathbf{v}_0 and \mathbf{i}_0 .

with the boundary conditions of vanishing heat flow and material flows, gives

$$(II.43) \quad \int_V T \sigma dV = \int_V \left\{ \Delta T \operatorname{div} \mathbf{J}_s + \sum_{k=1}^n \Delta \tilde{\mu}_k \operatorname{div} \mathbf{J}_k + \Delta \mathbf{v} \cdot \operatorname{Div} \mathbf{\Pi}^t - \right. \\ \left. - \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t + \Delta \mathbf{v} \cdot (c^{-1} \Delta \mathbf{i} \wedge \mathbf{B}) \right\} dV.$$

Using (II.4) and (II.32), and neglecting third order terms, (II.43) can be re-written as

$$(II.44) \quad T_0 \int_V \sigma dV = - \int_V \left\{ \Delta T (\partial \Delta s_v / \partial t + \operatorname{div} s_v \Delta \mathbf{v}) + \sum_{k=1}^n \Delta \tilde{\mu}_k (\partial \Delta \rho_k / \partial t + \right. \\ \left. + \operatorname{div} \rho_k \Delta \mathbf{v}) - \Delta \mathbf{v} \cdot \operatorname{Div} \mathbf{\Pi}^t + \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t - \Delta \mathbf{v} \cdot (c^{-1} \Delta \mathbf{i} \wedge \mathbf{B}) \right\} dV,$$

or, integrating again by parts and using the boundary conditions,

$$(II.45) \quad T_0 \int_V \sigma dV = - \int_V \left\{ \Delta T \partial \Delta s_v / \partial t + \sum_{k=1}^n \Delta \tilde{\mu}_k \partial \Delta \rho_k / \partial t + \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t - \right. \\ \left. - \Delta \mathbf{v} \cdot (s_v \operatorname{grad} \Delta T + \sum_{k=1}^n \rho_k \operatorname{grad} \Delta \tilde{\mu}_k - c^{-1} \Delta \mathbf{i} \wedge \mathbf{B} + \operatorname{Div} \mathbf{\Pi}^t) \right\} dV.$$

Applying (II.9) and the relation

$$(II.46) \quad s_v \operatorname{grad} T + \sum_{k=1}^n \rho_k \operatorname{grad} \tilde{\mu}_k = \operatorname{grad} p + \rho e \operatorname{grad} \varphi + \sum_{k=1}^n \rho_k \operatorname{grad} w_k,$$

which follows from the second law, the Gibbs-Duhem relations, and (II.31), equation (II.45) can be written as

$$(II.47) \quad T_0 \int_V \sigma dV = - \int_V \left\{ \Delta T \partial \Delta s_v / \partial t + \sum_{k=1}^n \Delta \tilde{\mu}_k \partial \Delta \rho_k / \partial t + \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t - \right. \\ \left. - \Delta \mathbf{v} \cdot (\rho e \operatorname{grad} \varphi + \sum_{k=1}^n \rho_k \operatorname{grad} w_k - c^{-1} \Delta \mathbf{i} \wedge \mathbf{B} + \operatorname{Div} \mathbf{P}^t) \right\} dV.$$

Applying (II.14) one has

$$(II.48) \quad T_0 \int_V \sigma dV = \int_V \left\{ \Delta T \partial \Delta s_v / \partial t + \sum_{k=1}^n \Delta \tilde{\mu}_k \partial \Delta \rho_k / \partial t - \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t + \right. \\ \left. + \Delta \mathbf{v} \cdot \partial \Delta \mathbf{g} / \partial t + \rho e \Delta \mathbf{v} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t \right\} dV.$$

Putting

$$(II.49) \quad \Delta \tilde{\mathbf{g}} = \Delta \mathbf{g} + \rho e c^{-1} \Delta \mathbf{A},$$

(II.48) becomes finally

$$(II.50) \quad T_0 \int_V \sigma dV = \\ = - \int_V (\Delta T \partial \Delta s_v / \partial t + \sum_{k=1}^n \Delta \tilde{\mu}_k \partial \Delta \rho_k / \partial t + \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t + \Delta \mathbf{v} \cdot \partial \Delta \tilde{\mathbf{g}} / \partial t) dV.$$

For an adiabatically insulated system, as no entropy is supplied to the system by its surroundings (cf. (II.28)), we have, from the integral of (II.27) and using Gauss' theorem, for the change of the total entropy per unit time dS/dt :

$$(II.51) \quad dS/dt = \int_V \sigma dV = \\ = - T_0^{-1} \int_V (\Delta T \partial \Delta s_v / \partial t + \sum_{k=1}^n \Delta \tilde{\mu}_k \partial \Delta \rho_k / \partial t + \Delta \mathbf{i} \cdot c^{-1} \partial \Delta \mathbf{A} / \partial t + \Delta \mathbf{v} \cdot \partial \Delta \tilde{\mathbf{g}} / \partial t) dV.$$

In order to apply fluctuation theory, the system must be energetically insulated, i.e. not only adiabatically, and it must be remarked that this condition for a system in which electromagnetic phenomena occur requires special attention. As it is shown in ^(5,10) the condition of energetical insulation does not change however the expression (II.51).

In fluctuation theory we strictly need dS/dt expressed as a function of independent state variables. The state variables Δs_v , $\Delta \rho_k$, $\Delta \mathbf{A}$ and $\Delta \tilde{\mathbf{g}}$ in (II.51) however are not all independent, because there exist $n+1$ relations (in the form of integral equations). These relations are the conservation of mass of the separate components and the conservation of total energy. As can easily be shown, these relations do not affect our results (cf. also ^(6-bis)).

It is clear that (II.51) has the form (I.19), hence the required form for the change of entropy of an energetically insulated system, which is appropriate for the application of fluctuation theory (cf. (I.15), (I.16)) and microscopic reversibility (cf. (I.23)-(I.25)). The variables Δs_v and $\Delta \rho_k$ are of the α -type, whereas the components of $c^{-1} \Delta \mathbf{A}$ and $\Delta \tilde{\mathbf{g}}$ are β -type variables. (ΔT and $\Delta \tilde{\mu}_k$ are the corresponding χ -type variables; the components of $\Delta \mathbf{i}$ and $\Delta \mathbf{v}$ are the corresponding γ -type variables).

5. - Fluctuations.

To these variables we apply the relations (I.15) or (I.16). This gives

$$(II.52) \quad \overline{\Delta s_v(\mathbf{r}) \Omega(\mathbf{r}') \Delta T(\mathbf{r}')} = kT_0 \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'),$$

$$(II.53) \quad \overline{\Delta s_v(\mathbf{r}) \Omega(\mathbf{r}') \Delta \tilde{\mu}_l(\mathbf{r}')} = 0, \quad (l=1, 2, \dots, n)$$

$$(II.54) \quad \overline{\Delta s_v(\mathbf{r}) \Omega(\mathbf{r}') \Delta i_j(\mathbf{r}')} = 0, \quad (j=1, 2, 3)$$

$$(II.55) \quad \overline{\Delta s_v(\mathbf{r}) \Omega(\mathbf{r}') \Delta v_j(\mathbf{r}')} = 0, \quad (j=1, 2, 3)$$

$$(II.56) \quad \overline{\Delta \rho_k(\mathbf{r}) \Omega(\mathbf{r}') \Delta T(\mathbf{r}')} = 0, \quad (k=1, 2, \dots, n)$$

$$(II.57) \quad \overline{\Delta \rho_k(\mathbf{r}) \Omega(\mathbf{r}') \Delta \tilde{\mu}_l(\mathbf{r}')} = kT_0 \delta_{kl} \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'), \quad (k, l=1, 2, \dots, n)$$

$$(II.58) \quad \overline{\Delta \rho_k(\mathbf{r}) \Omega(\mathbf{r}') \Delta i_j(\mathbf{r}')} = 0, \quad (k=1, 2, \dots, n; j=1, 2, 3)$$

$$(II.59) \quad \overline{\Delta \rho_k(\mathbf{r}) \Omega(\mathbf{r}') \Delta v_j(\mathbf{r}')} = 0, \quad (k=1, 2, \dots, n; j=1, 2, 3)$$

$$(II.60) \quad \overline{\Delta A_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta T(\mathbf{r}')} = 0, \quad (i=1, 2, 3)$$

$$(II.61) \quad \overline{\Delta A_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta \tilde{\mu}_l(\mathbf{r}')} = 0, \quad (i=1, 2, 3; l=1, 2, \dots, n)$$

$$(II.62) \quad \overline{\Delta A_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta i_j(\mathbf{r}')} = ckT_0 \delta_{ij} \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'), \quad (i, j=1, 2, 3)$$

$$(II.63) \quad \overline{\Delta A_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta v_j(\mathbf{r}')} = 0, \quad (i, j=1, 2, 3)$$

$$(II.64) \quad \overline{\Delta \tilde{g}_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta T(\mathbf{r}')} = 0, \quad (i=1, 2, 3)$$

$$(II.65) \quad \overline{\Delta \tilde{g}_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta \tilde{\mu}_l(\mathbf{r}')} = 0, \quad (i=1, 2, 3; l=1, 2, \dots, n)$$

$$(II.66) \quad \overline{\Delta \tilde{g}_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta i_j(\mathbf{r}')} = 0, \quad (i, j=1, 2, 3)$$

$$(II.67) \quad \overline{\Delta \tilde{g}_i(\mathbf{r}) \Omega(\mathbf{r}') \Delta v_j(\mathbf{r}')} = lT_0 \delta_{ij} \Omega(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'), \quad (i, j=1, 2, 3)$$

where k, l indicate chemical components and i, j Cartesian components. $\Omega(\mathbf{r})$ is an operator of the form (I.17).

The formulae (II.52)–(II.67) will be used in the calculation of the reciprocal relations between phenomenological coefficients.

6. - Microscopic Time Reversibility.

The equations of motion of the individual particles are invariant under time reversal, when also the external magnetic induction $\mathbf{B}_0(\mathbf{r})$ is reversed in every point. This property can be expressed with correlation functions by the

following expressions, which are examples of relations (I.23)-(I.25):

$$(II.68) \quad \overline{\Delta s_r(\mathbf{r})(\partial/\partial t)\Delta s_r(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta s_r(\mathbf{r}')(\partial/\partial t)\Delta s_r(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.69) \quad \overline{\Delta s_r(\mathbf{r})(\partial/\partial t)\Delta \rho_k(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta \rho_k(\mathbf{r}')(\partial/\partial t)\Delta s_r(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.70) \quad \overline{\Delta \rho_k(\mathbf{r})(\partial/\partial t)\Delta \rho_l(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta \rho_l(\mathbf{r}')(\partial/\partial t)\Delta \rho_k(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.71) \quad \overline{\Delta s_r(\mathbf{r})(\partial/\partial t)\Delta A_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = -\overline{\Delta A_j(\mathbf{r}')(\partial/\partial t)\Delta s_r(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.72) \quad \overline{\Delta \rho_k(\mathbf{r})(\partial/\partial t)\Delta A_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = -\overline{\Delta A_j(\mathbf{r}')(\partial/\partial t)\Delta \rho_k(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.73) \quad \overline{\Delta A_i(\mathbf{r})(\partial/\partial t)\Delta A_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta A_j(\mathbf{r}')(\partial/\partial t)\Delta A_i(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.74) \quad \overline{\Delta \tilde{g}_i(\mathbf{r})(\partial/\partial t)\Delta \tilde{g}_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta \tilde{g}_j(\mathbf{r}')(\partial/\partial t)\Delta \tilde{g}_i(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.75) \quad \overline{\Delta s_r(\mathbf{r})(\partial/\partial t)\Delta \tilde{g}_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = -\overline{\Delta \tilde{g}_j(\mathbf{r}')(\partial/\partial t)\Delta s_r(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.76) \quad \overline{\Delta \rho_k(\mathbf{r})(\partial/\partial t)\Delta \tilde{g}_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = -\overline{\Delta \tilde{g}_j(\mathbf{r}')(\partial/\partial t)\Delta \rho_k(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\},$$

$$(II.77) \quad \overline{\Delta A_i(\mathbf{r})(\partial/\partial t)\Delta \tilde{g}_j(\mathbf{r}')}\{\mathbf{B}_0, \mathbf{B}'_0\} = \overline{\Delta \tilde{g}_j(\mathbf{r}')(\partial/\partial t)\Delta A_i(\mathbf{r})}\{-\mathbf{B}_0, -\mathbf{B}'_0\}.$$

with $k, l = 1, 2, \dots, n$ and $i, j = 1, 2, 3$. The averages in the members of the equations (II.71), (II.72), (II.75) and (II.76) have opposite signs, the reason for this being, that Δs_r and $\Delta \rho_k$ are even functions of the particle velocities, whereas ΔA and $\Delta \tilde{g}$ are odd functions of these quantities (cf. chapter I, §§ 3, 4).

7. - Regression of Fluctuations.

In order to apply fluctuation theory, it is necessary to derive expressions for the decay of fluctuations, i.e. to express the time derivatives of the state variables Δs_r , $\Delta \rho_k$, ΔA and $\Delta \tilde{g}$, appearing in (II.51), as functions of the conjugate variables ΔT , $\Delta \tilde{\mu}_k$, $\Delta \mathbf{i}$ and $\Delta \mathbf{v}$ from (II.51).

In order to achieve this for $\partial A/\partial t$, we cannot just use one of the equations (II.34) or (II.39), since this would not give $\partial A/\partial t$ as a function of the conjugate variables mentioned. We can, however, proceed as follows. Introducing (II.40) into formula (II.11), we get

$$(II.78) \quad \mathbf{i} = \sum_{k=1}^{n-1} (e_k - e_n) \mathbf{J}_k.$$

Inserting (II.39) into (II.78) and then solving $e^{-1} \partial A/\partial t$, we find

$$(II.79) \quad e^{-1} \partial A/\partial t = -\mathbf{\Lambda}_{ee} \cdot \text{grad } T - \sum_{i=1}^{n-1} \mathbf{\Lambda}_{ei} \cdot \text{grad } (\tilde{\mu}_i - \tilde{\mu}_n) - \mathbf{\Lambda}_{ee} \cdot \mathbf{i} + e^{-1} (\mathbf{v} \wedge \mathbf{B}),$$

with the abbreviations

$$(II.80) \quad \mathbf{\Lambda}_{ee}^{-1} \equiv \sum_{k', k''=1}^{n-1} (e_{k'} - e_n)(e_{k''} - e_n) \mathbf{L}_{k'k''},$$

$$(II.81) \quad \mathbf{\Lambda}_{es} \equiv \sum_{k'=1}^{n-1} (e_{k'} - e_n) \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k's},$$

$$(II.82) \quad \mathbf{\Lambda}_{el} \equiv \sum_{k'=1}^{n-1} (e_{k'} - e_n) \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k'l}. \quad (l = 1, 2, \dots, n-1)$$

($\mathbf{\Lambda}_{ee}^{-1}$ in (II.80) means the inverse tensor of $\mathbf{\Lambda}_{ee}$). So, in this way $\partial A / \partial t$ has been found as a linear function of the proper variables.

Substituting (II.79) into (II.38) and (II.39), we obtain

$$(II.83) \quad \mathbf{J}_s = -\mathbf{\Lambda}_{ss} \cdot \text{grad } T - \sum_{l=1}^{n-1} \mathbf{\Lambda}_{sl} \cdot \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n) + \mathbf{\Lambda}_{se} \cdot \mathbf{i},$$

$$(II.84) \quad \mathbf{J}_k = -\mathbf{\Lambda}_{ks} \cdot \text{grad } T - \sum_{l=1}^{n-1} \mathbf{\Lambda}_{kl} \cdot \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n) + \mathbf{\Lambda}_{ke} \cdot \mathbf{i}, \quad (k = 1, 2, \dots, n-1)$$

with the abbreviations

$$(II.85) \quad \mathbf{\Lambda}_{ss} \equiv \mathbf{L}_{ss} - \sum_{k', k''=1}^{n-1} (e_{k'} - e_n)(e_{k''} - e_n) \mathbf{L}_{kk''} \cdot \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k's},$$

$$(II.86) \quad \mathbf{\Lambda}_{sl} \equiv \mathbf{L}_{sl} - \sum_{k', k''=1}^{n-1} (e_{k'} - e_n)(e_{k''} - e_n) \mathbf{L}_{kk''} \cdot \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k'l}, \quad (l = 1, 2, \dots, n-1)$$

$$(II.87) \quad \mathbf{\Lambda}_{se} \equiv \sum_{k'=1}^{n-1} (e_{k'} - e_n) \mathbf{L}_{sk'} \cdot \mathbf{\Lambda}_{ee},$$

$$(II.88) \quad \mathbf{\Lambda}_{ks} \equiv \mathbf{L}_{ks} - \sum_{k', k''=1}^{n-1} (e_{k'} - e_n)(e_{k''} - e_n) \mathbf{L}_{kk''} \cdot \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k's}, \quad (k = 1, 2, \dots, n-1)$$

$$(II.89) \quad \mathbf{\Lambda}_{kl} \equiv \mathbf{L}_{kl} - \sum_{k', k''=1}^{n-1} (e_{k'} - e_n)(e_{k''} - e_n) \mathbf{L}_{kk''} \cdot \mathbf{\Lambda}_{ee} \cdot \mathbf{L}_{k'l}, \quad (k, l = 1, 2, \dots, n-1)$$

$$(II.90) \quad \mathbf{\Lambda}_{ke} \equiv \sum_{k'=1}^{n-1} (e_{k'} - e_n) \mathbf{L}_{kk'} \cdot \mathbf{\Lambda}_{ee}.$$

We need to express the tensors \mathbf{L} explicitly in terms of the tensors $\mathbf{\Lambda}$. From (II.81), (II.82) and (II.85)–(II.90) we easily find

$$(II.91) \quad \mathbf{L}_{ss} = \mathbf{\Lambda}_{ss} + \mathbf{\Lambda}_{se} \cdot \mathbf{\Lambda}_{ee}^{-1} \cdot \mathbf{\Lambda}_{es},$$

$$(II.92) \quad \mathbf{L}_{sl} = \mathbf{\Lambda}_{sl} + \mathbf{\Lambda}_{se} \cdot \mathbf{\Lambda}_{ee}^{-1} \cdot \mathbf{\Lambda}_{el}, \quad (l = 1, 2, \dots, n-1)$$

$$(II.93) \quad \mathbf{L}_{ks} = \mathbf{\Lambda}_{ks} + \mathbf{\Lambda}_{ke} \cdot \mathbf{\Lambda}_{ee}^{-1} \cdot \mathbf{\Lambda}_{es}, \quad (k = 1, 2, \dots, n-1)$$

$$(II.94) \quad \mathbf{L}_{kl} = \mathbf{\Lambda}_{kl} + \mathbf{\Lambda}_{ke} \cdot \mathbf{\Lambda}_{ee}^{-1} \cdot \mathbf{\Lambda}_{el}. \quad (k, l = 1, 2, \dots, n-1)$$

Since we have n^2 tensors \mathbf{L} (i.e. $9n^2$ coefficients) and $(n+1)^2$ tensors $\mathbf{\Lambda}$ (i. e. $9(n+1)^2$ coefficients), there must exist $9(2n+1)$ relations between the $\mathbf{\Lambda}$'s.

We can now write the equations for the decay of fluctuations. Inserting (II.83) into (II.32) and neglecting second order terms in fluctuations, (which is in agreement with the fact, that we have neglected third order terms in equation (II.51)), we obtain

$$(II.95) \quad \partial \Delta s_v / \partial t = \operatorname{div} (\mathbf{\Lambda}_{ss} \cdot \operatorname{grad} \Delta T) + \sum_{l=1}^{n-1} \operatorname{div} \{ \mathbf{\Lambda}_{sl} \cdot \operatorname{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n) \} - \\ - \operatorname{div} (\mathbf{\Lambda}_{sv} \cdot \Delta \mathbf{i}) - \operatorname{div} (s_v^{(0)} \Delta \mathbf{v}),$$

where $s_v^{(0)}$ is the equilibrium value of s_v .

Introducing (II.84) into (II.4) (for $k = 1, 2, \dots, n-1$), we find

$$(II.96) \quad \partial \Delta \rho_k / \partial t = \operatorname{div} (\mathbf{\Lambda}_{ks} \cdot \operatorname{grad} \Delta T) + \sum_{l=1}^{n-1} \operatorname{div} \{ \mathbf{\Lambda}_{kl} \cdot \operatorname{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n) \} - \\ - \operatorname{div} (\mathbf{\Lambda}_{kv} \cdot \Delta \mathbf{i}) - \operatorname{div} (\rho_k^{(0)} \Delta \mathbf{v}), \quad (k = 1, 2, \dots, n-1)$$

with $\rho_k^{(0)}$ the equilibrium value of ρ_k . From (II.4), (II.40) and (II.84) we can also find an equation for $\partial \Delta \rho_n / \partial t$ as a function of the variables ΔT , $\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n$, $\Delta \mathbf{i}$ and $\Delta \mathbf{v}$. As a calculation however shows, this equation will not provide any new results in the derivation of reciprocal relations (see also § 8), and therefore we have not written it explicitly.

Equation (II.79), written in terms of fluctuations, becomes

$$(II.97) \quad e^{-1} \partial \Delta \mathcal{A} / \partial t = - \mathbf{\Lambda}_{es} \cdot \operatorname{grad} \Delta T - \sum_{l=1}^{n-1} \mathbf{\Lambda}_{el} \cdot \operatorname{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n) - \\ - \mathbf{\Lambda}_{ev} \cdot \Delta \mathbf{i} + e^{-1} (\Delta \mathbf{v} \wedge \mathbf{B}_0),$$

\mathbf{B}_0 being the external magnetic induction, which is supposed to be independent of the time.

Finally we find from (II.14), with (II.9), (II.41), (II.46) and (II.49)

$$(II.98) \quad \partial \Delta \tilde{g}_i / \partial t = - s_v^{(0)} \partial \Delta T / \partial x_i - \sum_{k=1}^n \rho_k^{(0)} \partial \Delta \tilde{\mu}_k / \partial x_i + e^{-1} (\Delta \mathbf{i} \wedge \mathbf{B}_0)_i + \\ + \rho^{(0)} e^{(0)} e^{-1} (\Delta \mathbf{v} \wedge \mathbf{B}_0)_i + \\ + \sum_{u=1}^3 (\partial / \partial x_u) \left\{ \sum_{m,n=1}^3 L_{(u)(mn)} \frac{1}{2} (\partial \Delta v_n / \partial x_m + \partial \Delta v_m / \partial x_n) \right\}, \quad (i = 1, 2, 3)$$

where $\rho^{(0)}$ and $e^{(0)}$ are the total density and the total charge per unit mass

respectively, in the state of thermodynamic equilibrium, and where $i = 1, 2, 3$ denote Cartesian components.

Equations (II.95), (II.96), (II.97) and (II.98) are the desired equations, which express the time derivatives of Δs_r , $\Delta \rho_k$, ΔA and $\Delta \tilde{g}$ in terms of ΔT , $\Delta \tilde{\mu}_k$, Δi and Δv .

Remark. In general the tensors \mathbf{L} , $\mathbf{\Lambda}$ and the coefficients $L_{(ij)(mn)}$ will depend on \mathbf{r} and $\mathbf{B}^*(\mathbf{r})$, where $\mathbf{B}^*(\mathbf{r})$ is the magnetic induction at the point \mathbf{r} , in a coordinate system, which moves with the same velocity as the (average) barycentric velocity \mathbf{v} in that point. In fluctuation theory, however, the (average) barycentric velocity is zero, and therefore $\mathbf{B}^*(\mathbf{r})$ becomes $\mathbf{B}_0(\mathbf{r})$.

8. - Reciprocal Relations for Heat Conduction, Diffusion and Cross-effects.

The reciprocal relations can now easily be obtained by the preceding results (cf. chapter I, § 5-6). One should insert the time derivatives of the state variables, expressed by the phenomenological laws (II.95)-(II.98), into the equations which express the macroscopic reversibility, and then use the results of the fluctuation theory.

We shall now derive reciprocal relations from the expressions (II.68)-(II.73) for microscopic reversibility. Substitution of (II.95) and (II.96) into (II.68), (II.69), and (II.70) gives:

$$(II.99) \quad \overline{\Delta s_r [\text{div}' \{ \mathbf{\Lambda}'_{rs}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' \} + \sum_{i=1}^{n-1} \text{div}' \{ \mathbf{\Lambda}'_{ri}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_i - \Delta \tilde{\mu}'_n) \} - \text{div}' \{ \mathbf{\Lambda}'_{re}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' \} - \text{div}' (s_r^{(0)} \Delta \mathbf{v}')] =$$

$$= \overline{\Delta s'_r [\text{div} \{ \mathbf{\Lambda}_{rs}(-\mathbf{B}_0) \cdot \text{grad} \Delta T \} + \sum_{i=1}^{n-1} \text{div} \{ \mathbf{\Lambda}_{ri}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_i - \Delta \tilde{\mu}_n) \} - \text{div} \{ \mathbf{\Lambda}_{re}(-\mathbf{B}_0) \cdot \Delta \mathbf{i} \} - \text{div} (s_r^{(0)} \Delta \mathbf{v})]},$$

$$(II.100) \quad \overline{\Delta s'_k [\text{div}' \{ \mathbf{\Lambda}'_{ks}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' \} + \sum_{i=1}^{n-1} \text{div}' \{ \mathbf{\Lambda}'_{ki}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_i - \Delta \tilde{\mu}'_n) \} - \text{div}' \{ \mathbf{\Lambda}'_{ke}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' \} - \text{div}' (s_k^{(0)} \Delta \mathbf{v}')] =$$

$$= \overline{\Delta s'_k [\text{div} \{ \mathbf{\Lambda}_{ks}(-\mathbf{B}_0) \cdot \text{grad} \Delta T \} + \sum_{i=1}^{n-1} \text{div} \{ \mathbf{\Lambda}_{ki}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_i - \Delta \tilde{\mu}_n) \} - \text{div} \{ \mathbf{\Lambda}_{ke}(-\mathbf{B}_0) \cdot \Delta \mathbf{i} \} - \text{div} (s_k^{(0)} \Delta \mathbf{v})]}, \quad (k = 1, 2, \dots, n-1)$$

$$\begin{aligned}
 \text{(II.101)} \quad & \overline{\Delta \varrho_k [\text{div}' \{ \mathbf{\Lambda}'_{ls}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' \} + \sum_{l'=1}^{n-1} \text{div}' \{ \mathbf{\Lambda}'_{l'l'}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_{l'} - \Delta \tilde{\mu}'_n) \} -} \\
 & \overline{\text{div}' \{ \mathbf{\Lambda}'_{le}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' \} - \text{div}' (\varrho_l^{(0)} \Delta \mathbf{v}')]} = \\
 & \overline{\Delta \varrho_l [\text{div} \{ \mathbf{\Lambda}_{ks}(-\mathbf{B}_0) \cdot \text{grad} \Delta T \} + \sum_{k'=1}^{n-1} \text{div} \{ \mathbf{\Lambda}_{kk'}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_{k'} - \Delta \tilde{\mu}_n) \} -} \\
 & \overline{\text{div} \{ \mathbf{\Lambda}_{ke}(-\mathbf{B}_0) \cdot \Delta \mathbf{i} \} - \text{div} (\varrho_k^{(0)} \Delta \mathbf{v})]}, \quad (k, l = 1, 2, \dots, n-1)
 \end{aligned}$$

where dashes indicate dependence on \mathbf{r}' .

We also could have taken (II.68), (II.69) and (II.70) for k and (or) l equal to n . Then we should have to substitute an expression for $\partial \Delta \varrho_n / \partial t$ similar to (II.96). As it is already remarked in § 7, we do not get new results in this way. Therefore we have only taken formulae with $k, l = 1, 2, \dots, n-1$. (For the same reason this is done below).

By means of (II.52)–(II.59), the equations (II.99)–(II.101) can be written as

$$\text{(II.102)} \quad \text{div}' \{ \mathbf{\Lambda}'_{ss}(\mathbf{B}'_0) \cdot \text{grad}' \delta(\mathbf{r} - \mathbf{r}') \} = \text{div} \{ \mathbf{\Lambda}_{ss}(-\mathbf{B}_0) \cdot \text{grad} \delta(\mathbf{r} - \mathbf{r}') \},$$

$$\begin{aligned}
 \text{(II.103)} \quad \text{div}' \{ \mathbf{\Lambda}'_{ks}(\mathbf{B}'_0) \cdot \text{grad}' \delta(\mathbf{r} - \mathbf{r}') \} &= \text{div} \left\{ \sum_{l=1}^{n-1} \mathbf{\Lambda}_{sl}(-\mathbf{B}_0) (\delta_{kl} - \delta_{kn}) \cdot \right. \\
 & \left. \text{grad} \delta(\mathbf{r} - \mathbf{r}') \right\}, \quad (k = 1, 2, \dots, n-1)
 \end{aligned}$$

$$\begin{aligned}
 \text{(II.104)} \quad \text{div}' \left\{ \sum_{l'=1}^{n-1} \mathbf{\Lambda}'_{l'l'}(\mathbf{B}'_0) \cdot (\delta_{kl'} - \delta_{kn}) \text{grad}' \delta(\mathbf{r} - \mathbf{r}') \right\} &= \\
 = \text{div} \left\{ \sum_{k'=1}^{n-1} \mathbf{\Lambda}_{kk'}(-\mathbf{B}_0) \cdot (\delta_{lk'} - \delta_{ln}) \text{grad} \delta(\mathbf{r} - \mathbf{r}') \right\}. & \quad (k = 1, 2, \dots, n-1)
 \end{aligned}$$

The δ -functions can be eliminated by multiplying with an arbitrary function $f(\mathbf{r})$ and integrating over \mathbf{r} . From (II.102) we obtain

$$\text{(II.105)} \quad \text{div} \{ \mathbf{\Lambda}_{ss}^\dagger(\mathbf{B}_0) \cdot \text{grad} f(\mathbf{r}) \} = \text{div} \{ \mathbf{\Lambda}_{ss}(-\mathbf{B}_0) \cdot \text{grad} f(\mathbf{r}) \},$$

where Kronecker δ 's have also been eliminated, and the left hand side of the equation has been twice partially integrated. The symbol \dagger indicates transposing of the Cartesian components. Since $f(\mathbf{r})$ is an arbitrary function, we obtain, equating the coefficients of the same first order derivative of $f(\mathbf{r})$,

$$\text{(II.106)} \quad \text{Div} \mathbf{\Lambda}_{ss}(\mathbf{B}_0) = \text{Div} \mathbf{\Lambda}_{ss}^\dagger(-\mathbf{B}_0).$$

Moreover, equating in (II.105) the coefficients of the same second order derivative of $f(\mathbf{r})$ we have

$$\text{(II.107)} \quad \mathbf{\Lambda}_{ss}(\mathbf{B}_0) + \mathbf{\Lambda}_{ss}^\dagger(\mathbf{B}_0) = \mathbf{\Lambda}_{ss}(-\mathbf{B}_0) + \mathbf{\Lambda}_{ss}^\dagger(-\mathbf{B}_0).$$

In an analogous way we obtain, from (II.103) and (II.104),

$$(II.108) \quad \begin{cases} \Lambda_{sk}(\mathbf{B}_0) + \Lambda_{sk}^+(\mathbf{B}_0) = \Lambda_{ks}(-\mathbf{B}_0) + \Lambda_{ks}^+(-\mathbf{B}_0) & \text{and} \\ \text{Div } \Lambda_{sk}(\mathbf{B}_0) = \text{Div } \Lambda_{ks}^+(-\mathbf{B}_0), & (k = 1, 2, \dots, n-1) \end{cases}$$

$$(II.109) \quad \begin{cases} \Lambda_{kl}(\mathbf{B}_0) + \Lambda_{kl}^+(\mathbf{B}_0) = \Lambda_{lk}(-\mathbf{B}_0) + \Lambda_{lk}^+(-\mathbf{B}_0) & \text{and} \\ \text{Div } \Lambda_{kl}(\mathbf{B}_0) = \text{Div } \Lambda_{lk}^+(-\mathbf{B}_0). & (k, l = 1, 2, \dots, n-1) \end{cases}$$

Substitution of (II.95)–(II.97) into (II.71)–(II.73) gives:

$$(II.110) \quad \begin{aligned} & \overline{c \Lambda_{s_i}[-\Lambda'_{es}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' - \sum_{l=1}^{n-1} \Lambda'_{el}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_l - \Delta \tilde{\mu}'_n) -} \\ & \overline{-\Lambda'_{es}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' + e^{-1}(\Delta \mathbf{v}' \wedge \mathbf{B}'_0)]_i} = \overline{-\Delta A'_j [\text{div} \{\Lambda_{es}(-\mathbf{B}_0) \cdot \text{grad } \Delta T\} +} \\ & \overline{+ \sum_{l=1}^{n-1} \text{div} \{\Lambda_{sl}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n)\} - \text{div} \{\Lambda_{se}(-\mathbf{B}_0) \cdot \Delta \mathbf{i}\} - \text{div} (s_e^{(0)} \Delta \mathbf{v})},} \\ & (j = 1, 2, 3) \end{aligned}$$

$$(II.111) \quad \begin{aligned} & \overline{c \Delta \rho_k[-\Lambda'_{es}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' - \sum_{l=1}^{n-1} \Lambda'_{el}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_l - \Delta \tilde{\mu}'_n) -} \\ & \overline{-\Lambda'_{es}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' + e^{-1}(\Delta \mathbf{v}' \wedge \mathbf{B}'_0)]_j} = \overline{-\Delta A_j(\mathbf{r}') [\text{div} \{\Lambda_{es}(-\mathbf{B}_0) \cdot \text{grad } \Delta T\} +} \\ & \overline{+ \sum_{l=1}^{n-1} \text{div} \{\Lambda_{kl}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n)\} - \text{div} \{\Lambda_{se}(-\mathbf{B}_0) \cdot \Delta \mathbf{i}\} - \text{div} (\rho_k^{(0)} \Delta \mathbf{v})},} \\ & (k = 1, 2, \dots, n-1; j = 1, 2, 3) \end{aligned}$$

$$(II.112) \quad \begin{aligned} & \overline{c \Delta A_i[-\Lambda'_{es}(\mathbf{B}'_0) \cdot \text{grad}' \Delta T' - \sum_{l=1}^{n-1} \Lambda'_{el}(\mathbf{B}'_0) \cdot \text{grad}' (\Delta \tilde{\mu}'_l - \Delta \tilde{\mu}'_n) -} \\ & \overline{-\Lambda'_{es}(\mathbf{B}'_0) \cdot \Delta \mathbf{i}' + e^{-1}(\Delta \mathbf{v}' \wedge \mathbf{B}'_0)]_j} = \overline{c \Delta A'_j [-\Lambda_{es}(-\mathbf{B}_0) \cdot \text{grad } \Delta T -} \\ & \overline{- \sum_{l=1}^{n-1} \Lambda_{sl}(-\mathbf{B}_0) \cdot \text{grad} (\Delta \tilde{\mu}_l - \Delta \tilde{\mu}_n) - \Lambda_{se}(-\mathbf{B}_0) \cdot \Delta \mathbf{i} - e^{-1}(\Delta \mathbf{v} \wedge \mathbf{B}_0)]_i},} \\ & (i, j = 1, 2, 3) \end{aligned}$$

where the indices i and j at square brackets denote the components of the vector between the brackets.

The equations (II.110)–(II.112) can be written, with (II.52)–(II.63), as

$$(II.113) \quad \begin{aligned} & \sum_{u=1}^3 A'_{es,ju}(\mathbf{B}'_0) (\partial/\partial x'_u) \delta(\mathbf{r} - \mathbf{r}') = \\ & = - \sum_{u,i=1}^3 (\partial/\partial x_u) \{A_{se,ui}(-\mathbf{B}_0) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}')\}, \end{aligned} \quad (j = 1, 2, 3)$$

$$(II.114) \quad \sum_{l=1}^{n-1} \sum_{u=1}^3 A'_{et,ju}(\mathbf{B}'_0)(\delta_{kl} - \delta_{kn})(\partial/\partial x'_u) \delta(\mathbf{r} - \mathbf{r}') = \\ = - \sum_{u,i=1}^3 (\partial/\partial x'_u) \{A_{ke,ui}(-\mathbf{B}_0) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}')\}, \quad (k=1, 2, \dots, n-1; j=1, 2, 3)$$

$$(II.115) \quad \sum_{u=1}^3 A'_{ee,ju}(\mathbf{B}'_0) \delta_{iu} \delta(\mathbf{r} - \mathbf{r}') = \sum_{u=1}^3 A_{ee,iu}(-\mathbf{B}_0) \delta_{ju} \delta(\mathbf{r} - \mathbf{r}'), \quad (i, j=1, 2, 3)$$

where i, j and u denote Cartesian components. Eliminating again Kronecker δ 's and δ -functions, we get

$$(II.116) \quad A_{ee,ju}(\mathbf{B}_0) = A_{ee,uj}(-\mathbf{B}_0), \quad \text{or: } \Lambda_{ee}(\mathbf{B}_0) = \Lambda_{ee}^{\dagger}(-\mathbf{B}_0),$$

$$(II.117) \quad A_{ek,ju}(\mathbf{B}_0) = A_{ke,uj}(-\mathbf{B}_0), \quad \text{or: } \Lambda_{ek}(\mathbf{B}_0) = \Lambda_{ke}^{\dagger}(-\mathbf{B}_0),$$

$$(II.118) \quad A_{ee,ji}(\mathbf{B}_0) = A_{ee,ij}(-\mathbf{B}_0), \quad \text{or: } \Lambda_{ee}(\mathbf{B}_0) = \Lambda_{ee}^{\dagger}(-\mathbf{B}_0),$$

with $i, j, u=1, 2, 3$ and $k=1, 2, \dots, n-1$.

The relations (II.116) and (II.117) are examples of reciprocal relations, which follow from expressions for the microscopic time reversibility relations containing both even and odd variables (*).

The reciprocal relations (II.107)–(II.109) and (II.116)–(II.118) have to be considered as intermediate results, because the Λ 's have only been introduced as convenient abbreviations in fluctuation theory. The desired reciprocal relations for \mathbf{L}_{ss} , \mathbf{L}_{sl} , \mathbf{L}_{ks} and \mathbf{L}_{kl} can be found from equations (II.91)–(II.94) with (II.107)–(II.109) and (II.116)–(II.118). From (II.91), (II.107), (II.116) and (II.118) follows

$$(II.119) \quad \mathbf{L}_{ss}(\mathbf{B}_0) + \mathbf{L}_{ss}^{\dagger}(\mathbf{B}_0) = [\Lambda_{ss}(\mathbf{B}_0) + \Lambda_{ss}^{\dagger}(\mathbf{B}_0)] + [\Lambda_{se}(\mathbf{B}_0) \cdot \Lambda_{ee}^{-1}(\mathbf{B}_0) \cdot \Lambda_{es}(\mathbf{B}_0) + \\ + \{\Lambda_{se}(\mathbf{B}_0) \cdot \Lambda_{ee}^{-1}(\mathbf{B}_0) \cdot \Lambda_{es}(\mathbf{B}_0)\}^{\dagger}] = [\Lambda_{ss}^{\dagger}(-\mathbf{B}_0) + \Lambda_{ss}(-\mathbf{B}_0)] + \\ + [\Lambda_{es}^{\dagger}(-\mathbf{B}_0) \cdot \Lambda_{ee}^{-1\dagger}(-\mathbf{B}_0) \cdot \Lambda_{se}^{\dagger}(-\mathbf{B}_0) + \Lambda_{es}^{\dagger}(\mathbf{B}_0) \cdot \Lambda_{ee}^{-1\dagger}(\mathbf{B}_0) \cdot \Lambda_{se}^{\dagger}(\mathbf{B}_0)] = \\ = [\Lambda_{ss}^{\dagger}(-\mathbf{B}_0) + \Lambda_{ss}(-\mathbf{B}_0)] + [\{\Lambda_{se}(-\mathbf{B}_0) \cdot \Lambda_{ee}^{-1}(-\mathbf{B}_0) \cdot \Lambda_{es}(-\mathbf{B}_0)\}^{\dagger} + \\ + \Lambda_{se}(-\mathbf{B}_0) \cdot \Lambda_{ee}^{-1}(-\mathbf{B}_0) \cdot \Lambda_{es}(-\mathbf{B}_0)] = \mathbf{L}_{ss}(-\mathbf{B}_0) + \mathbf{L}_{ss}^{\dagger}(-\mathbf{B}_0),$$

and, in an analogous way,

$$(II.120) \quad \text{Div } \mathbf{L}_{ss}(\mathbf{B}_0) = \text{Div } \mathbf{L}_{ss}^{\dagger}(-\mathbf{B}_0).$$

In the same way it is possible to derive from (II.92), (II.93), (II.108) and

(II.116)-(II.118)

$$(II.121) \quad \begin{cases} \mathbf{L}_{kk}(\mathbf{B}_0) + \mathbf{L}_{jk}^+(\mathbf{B}_0) = \mathbf{L}_{kk}(-\mathbf{B}_0) + \mathbf{L}_{kj}^+(-\mathbf{B}_0) & \text{and} \\ \text{Div } \mathbf{L}_{kk}(\mathbf{B}_0) = \text{Div } \mathbf{L}_{kk}^+(-\mathbf{B}_0), & (k = 1, 2, \dots, n-1) \end{cases}$$

and from (II.94), (II.109), (II.117) and (II.118)

$$(II.122) \quad \begin{cases} \mathbf{L}_{kl}(\mathbf{B}_0) + \mathbf{L}_{kl}^+(\mathbf{B}_0) = \mathbf{L}_{lk}(-\mathbf{B}_0) + \mathbf{L}_{lk}^+(-\mathbf{B}_0) & \text{and} \\ \text{Div } \mathbf{L}_{kl}(\mathbf{B}_0) = \text{Div } \mathbf{L}_{lk}^+(-\mathbf{B}_0). & (k, l = 1, 2, \dots, n-1) \end{cases}$$

With the convention of taking all phenomenological coefficients zero in empty space, and the fact that these coefficients do not depend on the shape of the sample it follows from (II.119)-(II.122)

$$(II.123) \quad \mathbf{L}_{kk}(\mathbf{B}_0) = \mathbf{L}_{kk}^+(-\mathbf{B}_0),$$

$$(II.124) \quad \mathbf{L}_{kk}(\mathbf{B}_0) = \mathbf{L}_{kk}^+(-\mathbf{B}_0), \quad (k = 1, 2, \dots, n-1)$$

$$(II.125) \quad \mathbf{L}_{kl}(\mathbf{B}_0) = \mathbf{L}_{lk}^+(-\mathbf{B}_0). \quad (k, l = 1, 2, \dots, n-1)$$

Taking into account (II.36) and (II.37), relations (II.124) and (II.125) are also valid for k and l , or both, equal to n .

Equation (II.123)-(II.125) are the reciprocal relations for heat conduction, diffusion and cross-effects in anisotropic media in the presence of an electromagnetic field.

9. - Reciprocal Relations for Viscosity.

Here we shall consider the microscopic time reversibilities (II.74)-(II.77).

Inserting equation (II.98) into (II.74), and using (II.64)-(II.66), we obtain

$$(II.126) \quad \overline{\Delta \tilde{g}_i [\varrho^{(0)} \epsilon^{(0)} c^{-1} (\Delta \mathbf{v}' \wedge \mathbf{B}'_0)_j]} + \overline{\sum_{\alpha=1}^3 (\partial/\partial x'_\alpha) \left\{ \sum_{m,n=1}^3 L'_{(\alpha i), (m n)}(\mathbf{B}'_0) \frac{1}{2} (\partial \Delta v'_n / \partial x'_m + \partial \Delta v'_m / \partial x'_n) \right\}} = \overline{\Delta \tilde{g}_j [-\varrho^{(0)} \epsilon^{(0)} c^{-1} (\Delta \mathbf{v} \wedge \mathbf{B}_0)_i + \sum_{\alpha=1}^3 (\partial/\partial x_\alpha) \left\{ \sum_{m,n=1}^3 L_{(\alpha i), (m n)}(-\mathbf{B}_0) \frac{1}{2} (\partial \Delta v_n / \partial x_m + \partial \Delta v_m / \partial x_n) \right\}}]. \quad (i, j = 1, 2, 3)$$

With (II.67) we find for (II.126)

$$\begin{aligned}
 \text{(II.127)} \quad & \sum_{u=1}^3 (\partial/\partial x'_u) \left[\sum_{m,n=1}^3 L'_{(uj),(mn)}(\mathbf{B}'_0) \{ \delta_{in} (\partial/\partial x'_m) \delta(\mathbf{r}-\mathbf{r}') + \delta_{im} (\partial/\partial x'_n) \delta(\mathbf{r}-\mathbf{r}') \} \right] = \\
 & = \sum_{u=1}^3 (\partial/\partial x_u) \left[\sum_{m,n=1}^3 L_{(uj),(mn)}(-\mathbf{B}_0) \{ \delta_{jn} (\partial/\partial x_m) \delta(\mathbf{r}-\mathbf{r}') + \delta_{jm} (\partial/\partial x_n) \delta(\mathbf{r}-\mathbf{r}') \} \right], \\
 & \qquad \qquad \qquad (i, j = 1, 2, 3)
 \end{aligned}$$

since a calculation shows that

$$\text{(II.128)} \quad \overline{\Delta \tilde{g}_i \rho^{(0)} e^{(0)} e^{-1} (\Delta \mathbf{v}' \wedge \mathbf{B}'_0)_j} = - \overline{\Delta \tilde{g}_j \rho^{(0)} e^{(0)} e^{-1} (\Delta \mathbf{v} \wedge \mathbf{B}_0)_i}$$

is an identity, when (II.67) is applied. Eliminating δ -functions and Kronecker δ 's we find from (II.127)

$$\text{(II.129)} \quad L_{(uj),(mi)}(\mathbf{B}_0) + L_{(mj),(ui)}(\mathbf{B}_0) = L_{(ui),(mj)}(-\mathbf{B}_0) + L_{(mi),(uj)}(-\mathbf{B}_0),$$

$$\text{(II.130)} \quad \sum_{m=1}^3 (\partial/\partial x_m) L_{(uj),(mi)}(\mathbf{B}_0) = \sum_{m=1}^3 (\partial/\partial x_m) L_{(mi),(uj)}(-\mathbf{B}_0),$$

with $i, j, m, u = 1, 2, 3$. With the usual boundary conditions (see § 8), we get

$$\text{(II.131)} \quad L_{(uj),(mi)}(\mathbf{B}_0) = L_{(mi),(uj)}(-\mathbf{B}_0). \quad (i, j, m, u = 1, 2, 3)$$

These are 15 reciprocal relations amongst the 36 viscosity coefficients. This leaves us with 21 independent coefficients.

When (II.95)–(II.98) are inserted into the equations (II.75)–(II.77) and when (II.52)–(II.67) are applied, we find three identities for (II.75), (II.76) and (II.77). As there arise no special difficulties, we shall not give an explicit calculation here.

10. – Case of Non-Vanishing Average Barycentric Motion.

So far we have found only reciprocal relations (equations (II.123)–(II.125) and (II.131)) for the case, in which the (average) barycentric motion is zero. When, however, the centre of gravity has an (average) velocity different from zero, these reciprocal relations still hold, when \mathbf{B}_0 is replaced by \mathbf{B}^* , i.e. the magnetic induction in a coordinate frame moving with the centre of gravity (cf. remark at the end of § 7). So we find

$$\text{(II.132)} \quad L_{ss}(\mathbf{B}^*) = L_{ss}^+(-\mathbf{B}^*),$$

$$\text{(II.133)} \quad L_{sk}(\mathbf{B}^*) = L_{ks}^+(-\mathbf{B}^*), \quad (k = 1, 2, \dots, n-1)$$

$$\text{(II.134)} \quad L_{kl}(\mathbf{B}^*) = L_{lk}^+(-\mathbf{B}^*), \quad (k, l = 1, 2, \dots, n-1)$$

$$\text{(II.135)} \quad L_{(uj)(mi)}(\mathbf{B}^*) = L_{(mi)(uj)}(-\mathbf{B}^*). \quad (i, j, m, u = 1, 2, 3)$$

These final results are the reciprocal relations for heat conduction (II.132), diffusion (II.134) and cross-effects (II.133) and also for viscosity (II.135) in mixtures of charged components with arbitrary movements in an electromagnetic field.

11. - Anisotropic Mixtures of Uncharged Components.

From the general case which has been treated in the foregoing one can easily derive the more particular cases in which the physical situation implies that not all the fluxes and forces are present.

The case of the anisotropic mixtures of n uncharged components, in which the phenomena of heat conduction, diffusion and cross-effects, and of viscous flow may occur, has been explicitly treated by DE GROOT and MAZUR (⁶) as a first example of their generalized Onsager theory. If we simply put $e_k = 0$, the phenomenological equations (II.38), (II.39) become

$$(II.136) \quad J_s = -L_{ss} \cdot \text{grad } T - \sum_{l=1}^{n-1} L_{sl} \cdot \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n),$$

$$(II.137) \quad J_k = -L_{ks} \cdot \text{grad } T - \sum_{l=1}^{n-1} L_{kl} \cdot \text{grad } (\tilde{\mu}_l - \tilde{\mu}_n), \quad (k=1, 2, \dots, n-1)$$

where now $\tilde{\mu}_l = \mu_l + w_l$ (the system may be subject to external conservative forces). The equations for the viscous flow already coincide with the corresponding equations which those authors have given. The reciprocal relations for the phenomenological coefficients, which have already been demonstrated in the previous sections, still hold.

12. - Galvanomagnetic and Thermomagnetic Phenomena in Anisotropic Metals.

Let us consider a system, consisting of a rigid ion lattice and of electrons, in an electromagnetic field and with a non uniform temperature. Equations (II.38), (II.39) reduce in this case, taking the barycentric velocity zero, to

$$(II.138) \quad J_s = -L_{ss} \cdot \text{grad } T - L_{se} \cdot \{ \text{grad } (\tilde{\mu}_e - \tilde{\mu}_i) - (e_e - e_i) e^{-1} \partial A / \partial t \},$$

$$(II.139) \quad J_e = -L_{ee} \cdot \text{grad } T - L_{ei} \cdot \{ \text{grad } (\tilde{\mu}_e - \tilde{\mu}_i) - (e_e - e_i) e^{-1} \partial A / \partial t \};$$

moreover (II.36) reads

$$(II.140) \quad J_i = -J_e.$$

(index e indicating electrons, index i ions). By introducing the electric current and with (II.140) we obtain

$$(II.141) \quad \mathbf{i} = e_e \rho_e \mathbf{v}_e + e_i \rho_i \mathbf{v}_i = (e_e - e_i) \mathbf{J}_e.$$

Using now the approximation $e_e \gg e_i$ (the charge density per unit mass of electrons is much larger than the charge density per unit mass of the ions), we can finally write

$$(II.142) \quad \mathbf{J}_e = -\mathbf{L}_{ee} \cdot \text{grad } T - \mathbf{L}_{ei} \cdot \{ \text{grad } (\tilde{\mu}_e - \tilde{\mu}_i) - e_e c^{-1} \partial \mathbf{A} / \partial t \},$$

$$(II.143) \quad \mathbf{i} = -e_e \mathbf{L}_{ee} \cdot \text{grad } T - e_e \mathbf{L}_{ei} \cdot \{ \text{grad } (\tilde{\mu}_e - \tilde{\mu}_i) - e_e c^{-1} \partial \mathbf{A} / \partial t \}.$$

Reciprocal relations (II.123)–(II.125) reduce to

$$(II.144) \quad \mathbf{L}_{ee}(\mathbf{B}_0) = \mathbf{L}_{ee}^{\dagger}(-\mathbf{B}_0), \quad \mathbf{L}_{ei}(\mathbf{B}_0) = \mathbf{L}_{ei}^{\dagger}(-\mathbf{B}_0), \quad \mathbf{L}_{ie}(\mathbf{B}_0) = \mathbf{L}_{ie}^{\dagger}(-\mathbf{B}_0).$$

These equations enable us to treat the galvanomagnetic and thermomagnetic phenomena in anisotropic metals. They will be reduced in the next chapter to the case of isotropic metals, in which situation galvano- and thermomagnetic phenomena are actually studied.

Remark. These phenomena have been already treated, from the point of view of thermodynamics of irreversible processes, by CALLEN⁽¹²⁾ and by MAZUR and PRIGOGINE⁽¹⁴⁾. Those authors, however, do not give a proof of the reciprocal relations: as it was usually done, they simply suppose that those relations are examples of the relations which ONSAGER⁽³⁾ derived for scalar processes from the property of microscopic reversibility.

The same case of an anisotropic metal in a magnetic field has been explicitly studied⁽¹¹⁾ by introducing the physical simplifications from the beginning in the fundamental laws. We should like to say, however, that the reduction of the general case to a more particular case, and the introduction of the simplifications in the phenomenological equations, allow sometimes a more complete description of the phenomena.

The equations of this section, as it may be easily seen, include the case of electric conduction in anisotropic crystals in a magnetic field at uniform temperature, which has been explicitly treated by MAZUR and DE GROOT⁽¹⁰⁾ by using their extension of Onsager's theory of reciprocal relations.

⁽¹²⁾ H. B. CALLEN: *Phys. Rev.*, **73**, 1349 (1948).

⁽¹³⁾ H. B. CALLEN: *Phys. Rev.*, **85**, 16 (1952).

⁽¹⁴⁾ P. MAZUR and I. PRIGOGINE: *Journ. Phys. et Radium*, **12**, 616 (1951).

CHAPTER III.

EXPLICIT EXPRESSIONS FOR THE MEASURABLE EFFECTS IN ISOTROPIC METALS

1. - Introduction.

In the preceding chapter we have derived the Onsager relations for heat conduction, electrical conduction and cross-effects in anisotropic metals in the presence of a magnetic field. The purpose of this chapter is to derive the expressions for the observable coefficients usually defined for the case of isotropic metals ⁽¹⁵⁾.

The coefficients for the galvanomagnetic and thermomagnetic effects have already been given in local form ^(12-14,1), i.e. the various relations between electric field, temperature gradient, heat and electrical flow are expressed in terms of the phenomenological coefficients at a certain point of the system. However these local coefficients do not necessarily correspond to the experimentally measured coefficients ⁽¹⁶⁻¹⁸⁾, because « heterogeneous and homogeneous thermoelectric effects » and Peltier effects may also play a role, in addition to the purely galvano- and thermomagnetic effects. Consequently, of course, the relations among the various effects have also to be modified.

Besides the effects which have already been studied in local form by other authors ⁽¹²⁻¹⁴⁾, mentioned above, we have considered also the analogous effects in a longitudinal magnetic field, and the Peltier effect in a transversal and longitudinal magnetic field ^(1,18,19). In particular we remark that Thomson's second relation is still valid in the presence of a magnetic field.

⁽¹⁵⁾ R. FIESCHI, S. R. DE GROOT and P. MAZUR: *Physica*, 20, 259 (1954).

⁽¹⁶⁾ W. MEISSNER: *Handbuch der Experimental-Physik*, 11 (Leipzig, 1935).

⁽¹⁷⁾ W. GERLACH: *Handbuch der Physik*, 13, Chapt. 6 (Berlin, 1928).

⁽¹⁸⁾ L. L. CAMPBELL: *Galvanomagnetic and thermomagnetic effects* (London, 1923).

⁽¹⁹⁾ G. LASKI: *Handbuch der Physik*, 13, Chapt. 5 (Berlin, 1928).

2. - Phenomenological Equations.

Let us consider an isotropic metal in a magnetic field \mathbf{B} , parallel to the z -axis. As can easily be seen, the phenomenological equations (II.142), (II.143) for this case, neglecting the time derivative of the vector potential $\partial\mathbf{A}/\partial t$, (i.e. assuming that the electron motion is sufficiently slow to allow us to neglect the effect of an induced magnetic field), can be written as (*)

$$(III.1) \quad i_x = -L_{ee,xx}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial x - L_{ee,xy}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial y - L_{es,xx} \partial T/\partial x - L_{es,xy} \partial T/\partial y,$$

$$(III.2) \quad i_y = L_{ee,xy}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial x - L_{ee,xx}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial y + L_{es,xy} \partial T/\partial x - L_{es,xx} \partial T/\partial y,$$

$$(III.3) \quad i_z = -L_{ee,zz}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial z - L_{es,zz} \partial T/\partial z,$$

$$(III.4) \quad J_{s,x} = -L_{se,xx}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial x - L_{se,xy}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial y - L_{ss,xx} \partial T/\partial x - L_{ss,xy} \partial T/\partial y,$$

$$(III.5) \quad J_{s,y} = L_{se,xy}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial x - L_{se,xx}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial y + L_{ss,xy} \partial T/\partial x - L_{ss,xx} \partial T/\partial y,$$

$$(III.6) \quad J_{s,z} = -L_{se,zz}e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i)/\partial z - L_{ss,zz} \partial T/\partial z,$$

The isotropy of the system requires, in addition to the following relations between the coefficients:

$$(III.7) \quad \begin{cases} L_{ee,xx} = L_{ee,yy}, & L_{es,xx} = L_{es,yy}, & L_{se,xx} = L_{se,yy}, & L_{ss,xx} = L_{ss,yy}, \\ L_{ee,xy} = -L_{ee,yx}, & L_{es,xy} = -L_{es,yx}, & L_{se,xy} = -L_{se,yx}, & L_{ss,xy} = -L_{ss,yx}, \end{cases}$$

which have already been taken into account in the equations (III.1)-(III.6), also that the coefficients $L_{ee,xx}$, $L_{ee,yy}$, $L_{se,xx}$, $L_{se,yy}$, $L_{ee,zz}$, $L_{es,zz}$, $L_{se,zz}$, and $L_{ss,zz}$ are even functions of the magnetic field, and that $L_{ee,xy}$, $L_{es,xy}$, $L_{se,xy}$ and $L_{ss,xy}$ are odd functions of the magnetic field.

Moreover the Onsager relations (II.144) hold between the coefficients:

$$(III.8) \quad L_{ee,ij}(\mathbf{B}) = L_{ee,ji}(-\mathbf{B}), \quad L_{es,ij}(\mathbf{B}) = L_{se,ji}(-\mathbf{B}), \quad L_{ss,ij}(\mathbf{B}) = L_{ss,ji}(-\mathbf{B}),$$

where i and j denote Cartesian components. Some of these relations already follow from the isotropy of the system, the really new relations being

$$L_{es,xx}(\mathbf{B}) = L_{se,xx}(-\mathbf{B}),$$

(*) For the sake of symmetry the coefficients L_{es} and L_{se} of equations (II.142, 143) have been multiplied by e_e and the coefficients L_{ee} of equation (II.143) have been multiplied by e_e^2 ; these constant parameters have been included in the coefficients of equations (III.1-6).

or, since $L_{se,xx}$ is an even function of \mathbf{B} ,

$$(III.9) \quad L_{es,xx}(\mathbf{B}) = L_{se,xx}(\mathbf{B});$$

$$L_{es,xy}(\mathbf{B}) = L_{se,yx}(-\mathbf{B}),$$

or, since $L_{se,xy}$ is an odd function of \mathbf{B} , and from (III. 7),

$$(III.10) \quad L_{es,xy}(\mathbf{B}) = L_{se,xy}(\mathbf{B});$$

$$L_{es,zz}(\mathbf{B}) = L_{se,zz}(-\mathbf{B}),$$

or, since $L_{se,zz}$ is an even function of \mathbf{B} ,

$$(III.10a) \quad L_{es,zz}(\mathbf{B}) = L_{se,zz}(\mathbf{B}).$$

Remark. Other authors (^{12-14,1}) have studied the case with fluxes and forces limited to the x - y coordinate plane. We have considered the more general case of fluxes and forces of arbitrary direction, in order to be able to deal also with the effects in a longitudinal magnetic field. The isotropy of the system requires that the coefficients with second sets of indices zx , zy , xz and yz vanish. So the equations (III.1), (III.2), (III.4) and (III.5) coincide with the equations which the quoted authors wrote down. In addition to these we have the equations (III.3) and (III.6), which are independent of the fluxes and forces in the x - y plane: they are the same equations which describe the thermoelectric effects, but the phenomenological coefficients are here of course functions of the magnetic field. These equations will enable us to treat the effects in a longitudinal magnetic field. (In the anisotropic case the effects in a longitudinal field contain of course also cross-terms, pertaining to the perpendicular directions).

MAZUR and PRIGOGINE (¹⁴) pointed out that a different form of the phenomenological equations provides a more convenient way to deal with the problem in the case of a metal. Their form differs in two respects from the form used above and in (¹²): 1st by choosing as independent variables the quantities which are directly controlled in the experiments (electric currents and temperature gradients), i.e. by changing the role of the electric flux and force, it is possible to obtain very simply the explicit expressions of the effects and the relations among them as functions of the phenomenological coefficients; 2nd moreover, a different choice of the fluxes and forces explained hereafter allows also the treatment of the effects in which the electric current does not vanish in the direction of the «adiabatical» insulation (*).

(*) In non-metallic systems the interchange of the role of electric flux and force is also preferable; but the different set of fluxes and forces is not suitable (¹³).

The new set of variables is obtained from the former set by a linear transformation which leaves the entropy production σ invariant. The entropy production (II.37) in our case is

$$(III.11) \quad \sigma = -T^{-1} \sum_{j=1}^3 [J_{e,j} (\partial T / \partial x_j) - J_{e,j} (\partial(\tilde{\mu}_e - \tilde{\mu}_i) / \partial x_j)].$$

The phenomenological equations (III.1)–(III.6), where i_j and $J_{e,j}$ are the flows, $-e_e^{-1} \partial(\tilde{\mu}_e - \tilde{\mu}_i) / \partial x_j$ and $\partial T / \partial x_j$ the corresponding forces, are based on this expression. With the linear transformations

$$(III.12) \quad \mathbf{J}_{\bar{q}} = T[\mathbf{J}_s - (s_e - s_i)\mathbf{J}_e],$$

where $\mathbf{J}_{\bar{q}}$ is called «reduced heat flow», s_e and s_i are the specific entropies of electrons and ions, (III.11) can be written as

$$(III.13) \quad \sigma = T^{-1} \sum_{j=1}^3 \left\{ -\mathbf{J}_{\bar{q},j} T^{-1} (\partial T / \partial x_j) + J_{e,j} \left\{ -(e_e - e_i) \partial \varphi / \partial x_j - [\partial(\mu_e - \mu_i) / \partial x_j]_{T=\text{const}} \right\} \right\},$$

or, since the total pressure and the concentrations of electrons and ions can be supposed uniform, $((\text{grad } \mu_e)_{T,P=\text{const}} = 0, (\text{grad } \mu_i)_{T,P=\text{const}} = 0)$ and with (II.141) and the approximation $e_e \gg e_i$,

$$(III.14) \quad \sigma = T^{-1} \sum_{j=1}^3 \left\{ -\mathbf{J}_{\bar{q},j} T^{-1} (\partial T / \partial x_j) + i_j E_j \right\},$$

where the electric field $\mathbf{E} = -\text{grad } \varphi$ has been introduced.

It is now possible to write linear phenomenological relations which express the fluxes i_i and $\mathbf{J}_{\bar{q},i}$ as functions of the forces $-T^{-1} \partial T / \partial x_i$ and E_i . As it has been said, however, it is convenient to express the variables $\mathbf{J}_{\bar{q},i}$ and E_i in terms of the other quantities.

$$(III.15) \quad E_x = L_{ee,xx} i_x + L_{ee,xy} i_y - L_{es,xx} T^{-1} \partial T / \partial x - L_{es,xy} T^{-1} \partial T / \partial y,$$

$$(III.16) \quad E_y = -L_{ee,xy} i_x + L_{ee,xx} i_y + L_{es,xy} T^{-1} \partial T / \partial x - L_{es,xx} T^{-1} \partial T / \partial y,$$

$$(III.17) \quad E_z = L_{ee,zz} i_z - L_{es,zz} T^{-1} \partial T / \partial z,$$

$$(III.18) \quad \mathbf{J}_{\bar{q},x} = L_{se,xx} i_x + L_{se,xy} i_y - L_{ss,xx} T^{-1} \partial T / \partial x - L_{ss,xy} T^{-1} \partial T / \partial y,$$

$$(III.19) \quad \mathbf{J}_{\bar{q},y} = -L_{se,xy} i_x + L_{se,xx} i_y + L_{ss,xy} T^{-1} \partial T / \partial x - L_{ss,xx} T^{-1} \partial T / \partial y,$$

$$(III.20) \quad \mathbf{J}_{\bar{q},z} = L_{se,zz} i_z - L_{ss,zz} T^{-1} \partial T / \partial z.$$

Here the isotropy of the system has already been taken into account; from this condition it follows also that $L_{se,xx}, L_{es,xx}, L_{se,xy}, L_{es,xy}, L_{ee,zz}, L_{es,zz}, L_{se,zz}$

and $L_{ss,zz}$ are even functions of the magnetic field, while $L_{ee,xy}$, $L_{es,xy}$, $L_{se,xy}$ and $L_{ss,xy}$ are odd functions of the magnetic field. The validity of the Onsager relations is conserved by a linear transformation of fluxes and forces (¹). Excluding the relations which are already given by the isotropy of the system, they read

$$(III.21) \quad L_{es,xx}(\mathbf{B}) = -L_{se,xx}(-\mathbf{B}) \{ = -L_{se,xx}(\mathbf{B}) \},$$

$$(III.22) \quad L_{es,xy}(\mathbf{B}) = -L_{se,yx}(-\mathbf{B}) \{ = -L_{se,xy}(\mathbf{B}) \},$$

$$(III.23) \quad L_{es,zz}(\mathbf{B}) = -L_{se,zz}(-\mathbf{B}) \{ = -L_{se,zz}(\mathbf{B}) \},$$

where the minus sign results from the interchange between the electrical flux and force.

With the aid of these relations the independent phenomenological coefficients reduce to six for the equations of the components in the x - y plane, perpendicular to the magnetic field: $L_{ee,xx}$, $L_{ee,xy}$, $L_{es,xx}$, $L_{es,xy}$, $L_{ss,xx}$ and $L_{ss,xy}$, and to three for the equations of the components in the direction of the magnetic field: $L_{ee,zz}$, $L_{es,zz}$ and $L_{ss,zz}$.

3. - Local Effects and Relations among Them.

The effects we study are defined in MEISSNER (¹⁶) (see also GERLACH (¹⁷)). The galvanomagnetic effects are caused by an electric current; the thermomagnetic effects are caused by a heat flow. In the transversal effects the primary current (heat or electric current) is perpendicular to the produced effect; in the longitudinal effects both variables have the same direction. An isothermal effect is defined in such a way that the temperature gradient in the direction perpendicular to the primary current is zero; for an adiabatic effect no heat is allowed to flow in the direction perpendicular to the primary current.

Symmetry arguments on the reversal of the magnetic field suggest that the transversal effects are in first approximation proportional to B , the longitudinal effects to B^2 . Several authors (^{12-18,1}) therefore divide the coefficients of the various effects (see following table) by B or B^2 respectively, in order to obtain new coefficients, which are «independent» of B . We prefer, however, not to express explicitly the dependence of the coefficients on the magnetic field, since the experimental deviations from the foregoing simple dependence are too relevant. The even or odd parity of the effects with respect to the magnetic field is already contained in the even or odd parity of the phenomenological coefficients, as is shown in the preceding section.

Below we give a table with the definitions of the various local effects (14, with a transversal magnetic field, of the theoretically possible $8!/2!3!3! = 560$, and 4 with a longitudinal magnetic field), and their local expressions in terms

TABLE I.

Galvanomagnetic effects						
	Name of the effect		definition	conditions	effect	
Transversal effects	I	Hall	isothermal: R_i^t	$\frac{E_y}{i_x}$	$i_y = 0, \frac{\partial T}{\partial x} = 0, \frac{\partial T}{\partial y} = 0.$	$-L_{ee,xy}$
	II		adiabatic: R_a^t			
	III	Ettingshausen: P^t	$\frac{\partial T/\partial y}{i_x}$	$i_y = 0, \frac{\partial T}{\partial x} = 0, J_{\bar{q},y} = 0.$	$-T \frac{L_{se,xy}}{L_{ss,xx}}$	
Longitudinal effects in a transversal field	VII	electric resistivity	isothermal: R_i^l	$\frac{E_x}{i_x}$	$i_y = 0, \frac{\partial T}{\partial x} = 0, \frac{\partial T}{\partial y} = 0.$	$L_{ee,xx}$
	VIII		adiabatic: R_a^l			
	IX	Nernst	isothermal: P_i^l	$\frac{\partial T/\partial x}{i_x}$	$i_y = 0, J_{\bar{q},x} = 0, \frac{\partial T}{\partial y} = 0.$	$T \frac{L_{se,xx}}{L_{ss,xx}}$
	X		adiabatic: P_a^l			
Longitudinal effects in a longitudinal field	XV	electric resistivity: R^{ls}	$\frac{E_z}{i_z}$	$\frac{\partial T}{\partial z} = 0.$	$L_{ee,zz}$	
	XVI	P^{ss}	$\frac{\partial T/\partial z}{i_z}$	$J_{\bar{q},z} = 0.$	$T \frac{L_{se,zz}}{L_{ss,zz}}$	

TABLE II.

Thermomagnetic effects						
	Name of the effect		definition	conditions	effect	
Transversal effects	IV	Righi-Leduc: S^t	$\frac{\partial T/\partial y}{\partial T/\partial x}$	$i_x = 0, i_y = 0, J_{\bar{y},y} = 0.$	$\frac{L_{ss,xy}}{L_{ss,xx}}$	
	V	Nernst	$\frac{E_y}{\partial T/\partial x}$	isothermal: Q_i^s	$i_x = 0, i_y = 0, \frac{\partial T}{\partial y} = 0.$	$T^{-1}L_{es,xy}$
	VI			adiabatic: Q_a^t	$i_x = 0, i_y = 0, J_{\bar{y},y} = 0.$	$T^{-1}\left(L_{es,xy} - \frac{L_{es,xx}L_{ss,xy}}{L_{ss,xx}}\right)$
Longitudinal effects in a transversal field	XI	heat conductivity	$-\frac{J_{\bar{y},x}}{\partial T/\partial x}$	isothermal: λ_i	$i_x = 0, i_y = 0, \frac{\partial T}{\partial y} = 0.$	$T^{-1}L_{ss,xx}$
	XII			adiabatic: λ_a	$i_x = 0, i_y = 0, J_{\bar{z},y} = 0.$	$T^{-1}\left(L_{ss,xx} + \frac{L_{ss,xy}^2}{L_{ss,xx}}\right)$
	XIII	Ettingshausen-Nernst	$\frac{E_x}{\partial T/\partial x}$	isothermal: Q_i^t	$i_x = 0, i_y = 0, \frac{\partial T}{\partial y} = 0.$	$-T^{-1}L_{es,xx}$
	XIV			adiabatic: Q_a^t	$i_x = 0, i_y = 0, J_{\bar{y},y} = 0.$	$-T^{-1}\left(L_{es,xx} + \frac{L_{es,xy}L_{ss,xy}}{L_{ss,xx}}\right)$
Longitudinal effects in a longitudinal field	XVII	heat conductivity: λ^{1B}	$-\frac{J_{\bar{y},z}}{\partial T/\partial z}$	$i_z = 0.$	$T^{-1}L_{ss,zz}$	
	XVIII	homogeneous thermoelectric effect: Q^{1B}	$\frac{E_z}{\partial T/\partial z}$	$i_z = 0.$	$-T^{-1}L_{es,zz}$	

of the phenomenological coefficients (¹²⁻¹⁴), which are easily derived from the equations (III.15)–(III.20).

When the isotropy of the system is taken into account, the 14 effects with the transversal field are expressed in terms of 9 independent phenomenological coefficients (cf. table); hence 5 relations exist, connecting the effects with each other, which are simply due to the symmetry of the system:

$$(III.24) \quad R_a^i - R_i^a = -Q_i^a P^i,$$

$$(III.25) \quad \lambda_a - \lambda_i = (S^i)^2 \lambda_i,$$

$$\left. \begin{aligned} (III.26) \quad R_a^i - R_i^a &= Q_i^a P^i, \\ (III.27) \quad Q_a^i - Q_i^a &= Q_i^a S^i, \end{aligned} \right\} \text{(Heulinger relations)}$$

$$(III.28) \quad Q_a^i - Q_i^a = -Q_i^a S^i.$$

Moreover, the Onsager relations (III.21) and (III.22) reduce the number of the independent coefficients to 6; we then have among the effects 3 more relations:

$$(III.29) \quad \lambda_i P^i = T Q_i^a, \quad \text{(Bridgman relation)}$$

$$(III.30) \quad \lambda_i P_i^a = T Q_i^a,$$

$$(III.31) \quad \lambda_a P_a^i = T Q_a^i.$$

Owing to the Onsager relation (III.23), the 4 effects with the longitudinal field are expressed in terms of 3 independent phenomenological coefficients; hence one relation exists among them:

$$(III.32) \quad \lambda^{iB} P^{iB} = T Q^{iB}.$$

4. - Measurable Effects.

Let us consider a system consisting of a metallic sample *A* and of the metallic wires *B*, which connect two corresponding points on opposite faces of the sample with a condenser *C* (fig. 1). We call: $(\Delta\varphi)_i = (\varphi_1 - \varphi_2)_i$ the potential difference which is measured (for instance) with a condenser connected

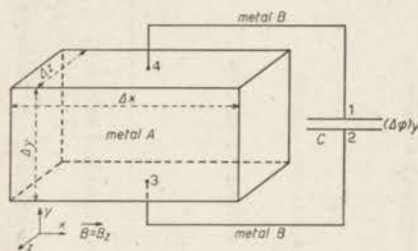


Fig. 1. - Sample with connecting wires.

with the corresponding points on the faces parallel to the plane $x_j x_k$ ($x_1 = x$, $x_2 = y$, $x_3 = z$; $i, j, k = 1, 2, 3$; $i \neq j \neq k$) (the figure illustrates the case $i \equiv y$); $(\Delta T)_i$ the temperature difference between the corresponding points on the faces parallel to the plane $x_j x_k$ ($i \neq j \neq k$); I_i the total electric current which is measured in the direction x_i ; $I_{a,i}$ the total « re-

duced heat flow » which flows in the direction x_i . Moreover we suppose that i_i , $J_{\bar{q},i}$, $\partial\varphi/\partial x_i$ and $\partial T/\partial x_i$ are uniform inside the metal A . Then the following relations hold between the above defined measurable quantities and the corresponding «local» variables:

$$(III.33) \quad (\varphi_4 - \varphi_3)_i = \int_{\Delta x_i} (\partial\varphi/\partial x_i) dx_i = \Delta x_i (\partial\varphi/\partial x_i),$$

$$(III.34) \quad (\Delta T)_i = \int_{\Delta x_i} (\partial T/\partial x_i) dx_i = \Delta x_i (\partial T/\partial x_i),$$

$$(III.35) \quad I_i = \int_{\Delta x_j \Delta x_k} i_i dx_j dx_k = \Delta x_j \Delta x_k i_i, \quad (i \neq j \neq k)$$

$$(III.36) \quad I_{\bar{q},i} = \int_{\Delta x_j \Delta x_k} J_{\bar{q},i} dx_j dx_k = \Delta x_j \Delta x_k J_{\bar{q},i}. \quad (i \neq j \neq k)$$

In the experimental apparatus one has, besides the sample A , which is placed in the magnetic field \mathbf{B} , wires of a different metal B and junctions of the two different metals (Fig. 1: points 3 and 4). Consequently one should pay attention to the thermoelectric effects which may be superimposed on the pure galvano- and thermomagnetic effects.

When the temperature in the wires and at the junctions is different, a condenser records, in addition to the potential difference of galvano- or thermomagnetic origin, a thermoelectric potential difference which is given by the following two effects ⁽¹⁾.

1) The «homogeneous thermoelectric effect», i.e. the potential difference inside the single wires, is given by

$$(III.37) \quad \varphi_a - \varphi_b = -Q_B^{**}(T_a - T_b)/eT,$$

where the indices a and b indicate two points of a wire, Q^{**} is the «reduced heat of transfer» for the electrons in the metal B (i.e. the reduced heat transported by the unit of mass of the electrons in the state of uniform temperature, which can be expressed by the coefficients of the phenomenological equations for metal B) (*).

(*) In the literature two sets of «heats of transfer» are used ⁽²⁰⁾: one of the sets consists of n quantities; each of these quantities may be interpreted as the heat transported per unit flow of matter of a certain chemical component. The other set consists of $n-1$ quantities, where each quantity may be interpreted as the heat transported per unit flow of matter of a certain chemical component relative to the barycentric motion. Since in our case $c_e \ll c_i$ (c_e is the concentration of electrons, c_i the concentration of ions), it is easily seen ⁽²⁰⁾ that the «heats of transfer» of the latter set coincide with the first $n-1$ heats of transfer of the first set mentioned (in our case $n=2$). Moreover, since relative and absolute flows coincide, the corresponding two kinds of «reduced heat of transfer» also coincide, and no further specification is necessary.

⁽²⁰⁾ G. A. KLUITENBERG, S. R. DE GROOT and P. MAZUR: *Physica*, **19**, 1079 (1953), § 6.

2) The « heterogeneous thermoelectric effect », i.e. the potential difference at the junction of two different metals A and B at the temperature T , is given by

$$(III.38) \quad (\varphi_A - \varphi_B)_T = e^{-1}(\mu_A - \mu_B)_T,$$

where μ_A and μ_B are the chemical potentials of electrons in the two metals (+).

The general equation for the resulting potential is obtained by adding up the homogeneous and heterogeneous potential differences in the circuit. One then obtains, for (III.33), (III.37) and (III.38), (Fig. 1),

$$(III.39) \quad (\Delta\varphi)_i = (\varphi_1 - \varphi_2)_i = (\varphi_1 - \varphi_4)_B + (\varphi_B - \varphi_A)_{T_1} + (\varphi_4 - \varphi_3)_A + \\ + (\varphi_A - \varphi_B)_{T_2} + (\varphi_3 - \varphi_2)_B = e^{-1}T^{-1}Q_B^{**}(T_4 - T_1) + e^{-1}(\mu_A - \mu_B)T_4 + \\ + \int_{\Delta x_i} (\partial\varphi/\partial x_i) dx_i + e^{-1}(\mu_B - \mu_A)_{T_2} + e^{-1}T^{-1}Q_B^{**}(T_2 - T_3) = \\ = e^{-1}T^{-1}Q_B^{**}(T_4 - T_1 + T_2 - T_3) + e^{-1}[\partial(\mu_A - \mu_B)/\partial T](T_4 - T_3) + \\ + (\partial\varphi/\partial x_i) \Delta x_i = e^{-1}T^{-1}Q_B^{**}(T_4 - T_1 + T_2 - T_3) + \\ + e^{-1}(s_B - s_A)(T_4 - T_3) + (\partial\varphi/\partial x_i) \Delta x_i.$$

The quantities s_A and s_B are the specific entropies of electrons in the metals A and B , and in the last step of the derivation Gibbs' equation has been used.

If the temperature gradient vanishes in the direction in which the potential difference is measured, ($T_1 = T_2 = T_3 = T_4$), the « homogeneous thermoelectric effect » also vanishes, the « heterogeneous effects » at the two junctions are equal and with opposite sign, and one has simply

$$(III.40) \quad (\Delta\varphi)_i = (\partial\varphi/\partial x_i) \Delta x_i = -E_i \Delta x_i.$$

The isothermal Hall (I) and Nernst (V) effects, and the isothermal (VII) and adiabatic (VIII) electrical resistivity belong to this case.

For the adiabatic Hall (II) and Nernst (VI) effects, one has $T_3 \neq T_4$, but $T_1 = T_4$ and $T_2 = T_3$ (from the adiabatical insulation condition for the y direction). The homogeneous thermoelectric effect then vanishes and (III.39) becomes

$$(III.41) \quad (\Delta\varphi)_i = e^{-1}(s_B - s_A)(T_4 - T_3) - E_i \Delta x_i.$$

For the isothermal (XIII) and adiabatic (XIV) Ettingshausen-Nernst effects

() Here and in the following we let $e_e = e$.

the homogeneous thermoelectric effect can also be present, since the adiabatical insulation in the direction in which the electric field is measured is no longer necessary; (III.41) is then again valid only for the case that the temperature gradient is zero in the wires which connect the metal *A* with the condenser. In the following we shall consider this case in order to have consistency in the definitions and more simplicity in the relations among the various effects. In § 6, however, to treat the Peltier effect, it is convenient to consider the more general case in which a temperature gradient in the wires is also present.

If sample and wires are made of the same metal, the heterogeneous thermoelectric effect is the potential difference at the «junctions» between the metal inside the magnetic field and the metal outside: s_a is then the specific entropy of electrons for the metal inside the magnetic field, while s_b is the specific entropy of electrons in the metal without magnetic field (see the end of § 6); T_3 and T_4 are the temperature at the points where the magnetic field drops to zero.

If the boundary of the magnetic field does not coincide with the junctions between the two metals, but part of metal *A* is left outside the field, one has 4 discontinuity points for the electric potential (fig. 2: points 1, 2, 3 and 4), and homogeneous thermoelectric effects both in the wires *B* and in the parts of *A* outside the field (fig. 2: the dotted lines indicate the boundaries of the magnetic field).

It is now easy to give the relations between measurable and local effects. The coefficients with an upper bar indicate measurable coefficients, while without the bar they indicate local coefficients.

The isothermal Hall coefficient (*I*) is defined by $\bar{R}'_i \equiv -(\Delta\varphi)_y \Delta z / I_x$, when $I_y = 0$, $(\Delta T)_x = 0$ and $(\Delta T)_y = 0$. From (III.35) and (III.40) one has: $\bar{R}'_i = E_y \Delta y \Delta z / i_x \Delta y \Delta z = R'_i$. In a similar way it is immediately seen that the following observable effects coincide with the local effects. (For the sake of brevity we shall not write the conditions which define every observable effect, as they coincide with the conditions for the corresponding local effect). Isothermal Nernst coefficient (*V*): $\bar{Q}'_i \equiv -(\Delta\varphi)_y \Delta x / (\Delta T)_x \Delta y = Q'_i$. (As a matter of fact temperature and potential differences in the *x* (longitudinal) direction are not measured at the ends of the sample *A*. In these cases, hence Δx is the distance between the points where the measurements are performed (fig. 2, points *a* and *b*)). Ettingshausen coefficient (*III*): $\bar{P}' \equiv (\Delta T)_y \Delta z / I_x = P'$. Righi-Leduc coefficient (*IV*): $\bar{S}' \equiv (\Delta T)_x \Delta x / (\Delta T)_x \Delta y = S'$. Isothermal (*VII*)

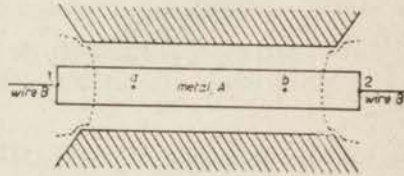


Fig. 2. - Sample in magnetic field. (Point 3 is at the left-hand dotted line in the metal; point 4 is at the right-hand dotted line in the metal).

and adiabatic (VIII) electric resistivity: $\bar{R}^t \equiv -(\Delta\varphi)_x \Delta y \Delta z / I_x \Delta x$; $R_i^t = R_i^t$, $\bar{R}_a^t = R_a^t$. Isothermal (XI) and adiabatic (XII) heat conductivity: $\bar{\lambda} \equiv -I_{\bar{y},x} \Delta x / (\Delta T)_x \Delta y \Delta z$; $\bar{\lambda}_i = \lambda_i$, $\bar{\lambda}_a = \lambda_a$.

For the adiabatic Hall effect (II), as we have said in the foregoing, the influence of the potential difference at one junction is no longer compensated by the potential difference at the other junction, since the temperature at the two junctions is not the same. So we have, from (III.41),

$$\begin{aligned} \bar{R}_a^t &\equiv -(\Delta\varphi)_y \Delta z / I_x = (\Delta z / i_x \Delta y \Delta z) [E_y \Delta y + e^{-1}(s_B - s_A)\{-\Delta T\}_y] = \\ &= R_a^t + e^{-1}(s_A - s_B)\{(\Delta T)_y / i_x \Delta y\}, \end{aligned}$$

or, for the definition of effect (III) in the table,

$$(III.42) \quad \bar{R}_a^t = R_a^t + e^{-1}(s_A - s_B)P^t.$$

In an analogous way one finds, for the adiabatic Nernst coefficient (VI),

$$(III.43) \quad \bar{Q}_a^t \equiv -(\Delta\varphi)_y \Delta x / (\Delta T)_x \Delta y = Q_a^t + e^{-1}(s_A - s_B)S^t,$$

where the definition of effect (IV) in the table has been used. This correction for the measurable adiabatic Nernst coefficient has been given already by CAMPBELL⁽¹⁸⁾.

For the longitudinal isothermal Etingshausen-Nernst coefficient (XIII) one has

$$(III.44) \quad \bar{Q}_i^t \equiv -(\Delta\varphi)_x / (\Delta T)_x = Q_i^t + e^{-1}(s_A - s_B),$$

and for the longitudinal adiabatic Etingshausen-Nernst coefficient (XIV)

$$(III.45) \quad \bar{Q}_a^t = Q_a^t + e^{-1}(s_A - s_B).$$

As we have remarked, these last two results are valid for the case in which the temperature gradient is zero in the wires. If the temperature gradient is non-vanishing and uniform (and so also $T_1 = T_2$), one has from (III.31)

$$(III.46) \quad \bar{Q}_i^t = Q_i^t + \{e^{-1}(s_A - s_B) - e^{-1}T^{-1}Q_B^{**}\},$$

and

$$(III.47) \quad \bar{Q}_a^t = Q_a^t + \{e^{-1}(s_A - s_B) - e^{-1}T^{-1}Q_B^{**}\}.$$

The longitudinal isothermal (IX) and adiabatic (X) Nernst effects are the only two effects in which the electric current in the direction, in which one

measures the temperature difference, does not vanish. One has therefore an evolution of heat at the junctions, which modifies the temperature difference due to the pure galvanomagnetic effect. However, the effect of heating at the junction should be corrected with suitable experimental arrangement, as it would be complicated to consider explicitly its influence on the expressions of the two galvanomagnetic coefficients. Apart from that, the experimental coefficients coincide with the local ones. The conditions supposed in this case are hardly to be obtained practically, as we must assume the possibility of the existence of an electric current without an accompanying «reduced heat flow». Nevertheless, the case is of theoretical interest. Longitudinal isothermal and adiabatic Nernst coefficients:

$$\bar{P}^l = (\Delta T)_x \Delta y \Delta z / I_x \Delta x; \quad \bar{P}_i^l = P_i^l, \quad \bar{P}_a^l = P_a^l.$$

For the longitudinal effects in a longitudinal magnetic field again the same considerations hold as for the corresponding longitudinal effects in a transversal field. Two of them (XV) and (XVII) are unchanged: $\bar{R}^{lB} = R^{lB}$ and $\bar{\lambda}^{lB} = \lambda^{lB}$. The thermoelectric power (XVIII) $\bar{Q}^{lB} = -(\Delta\varphi)_z / (\Delta T)_z$ is given by

$$(III.48) \quad \bar{Q}^{lB} = Q^{lB} + e^{-1}(s_A - s_B),$$

if the temperature gradient is zero in the wires, and by

$$(III.49) \quad \bar{Q}^{lB} = Q^{lB} + \{e^{-1}(s_A - s_B) - e^{-1}T^{-1}Q_B^{**}\},$$

if the temperature gradient is non-vanishing and uniform. The coefficient \bar{P}^{lB} (XVI) is again affected by the influence of an evolution of heat at the junctions, which cannot be expressed explicitly.

5. - Relations Among the Measurable Coefficients.

We have seen that the local expressions of the four effects II, VI, XIII and XIV, where the temperature gradient does not vanish in the direction in which the electric field is measured, must be modified, because for these cases a thermoelectric potential difference is superimposed on the galvano- or thermomagnetic potential difference. Consequently, some of the relations among the various effects are also modified.

The relations (III.24), (III.27) and (III.28) remain unmodified because the local and the measurable coefficients, which appear in them, coincide.

It is easy to see that the relations (III.29), (III.30) and (III.31), expressed in the measurable coefficients, remain unchanged, although the expressions for the measurable coefficients are different from the expressions for the local coefficients.

Relations (III.25) and (III.26) are no longer valid when the measurable coefficients are substituted for the local coefficients. The relations then become

$$(III.50) \quad \bar{\lambda}_i \bar{P}_i^t = T \bar{Q}_i^t + e^{-1}(s_A - s_B)$$

and

$$(III.51) \quad \bar{\lambda}_a \bar{P}_a^t = T \bar{Q}_a^t + e^{-1}(s_A - s_B),$$

or, by eliminating the specific entropies,

$$(III.52) \quad \bar{\lambda}_i \bar{P}_i^t - \bar{\lambda}_a \bar{P}_a^t = T(\bar{Q}_i^t - \bar{Q}_a^t).$$

Also the relation (III.32) for the longitudinal effects in a longitudinal field is not valid any more for the measurable effects. Instead of it we have

$$(III.53) \quad \bar{\lambda}^{1B} \bar{P}^{1B} = T \bar{Q}^{1B} + e^{-1}(s_A - s_B).$$

In this way finally all relations among measurable effects have been found.

6. - Peltier Effect in a Magnetic Field and Thomson's second Relation.

In this section we wish to extend the theory of thermoelectricity ⁽¹⁾ to the case in which a magnetic field is present.

In order to study the Peltier effect in a magnetic field it is convenient to extend the definition of « reduced heat of transfer ». In a transversal magnetic field we define an « isothermal reduced heat of transfer » $(Q^{**})_i^{tB} = e^{-1}(J_{\bar{v},x}/i_x)_i^{tB}$, with the conditions $i_y = 0$, $\partial T/\partial x = 0$, $\partial T/\partial y = 0$; and an « adiabatical reduced heat of transfer », $(Q^{**})_a^{tB} = e^{-1}(J_{\bar{v},x}/i_x)_a^{tB}$, with the conditions $i_y = 0$, $\partial T/\partial x = 0$, $J_{\bar{v},y} = 0$. From the equations (III.18) and (III.19) we have then $(Q^{**})_i^{tB} = e^{-1}L_{ee,xx}$, or, with the Onsager relation (III.21),

$$(III.54) \quad (Q^{**})_i^{tB} = -e^{-1}L_{es,xx};$$

$(Q^{**})_a^{tB} = e^{-1}(L_{ee,xx} + L_{ss,xy}L_{se,xy}/L_{ss,xx})$, or, with the Onsager relations (III.21) and (III.22),

$$(III.55) \quad (Q^{**})_a^{tB} = e^{-1}(-L_{es,xx} - L_{ss,xy}L_{es,xy}/L_{ss,xx}).$$

In a longitudinal magnetic field we define the reduced heat of transfer $(Q^{**})^{1B} = e^{-1}(J_{\bar{v},z}/i_z)^{1B}$, with the condition $\partial T/\partial z = 0$. From equation (III.20)

we have

$$(Q^{**})^{iB} = e^{-1}L_{se,zz}, \text{ or, with the Onsager relation (III.23),}$$

$$(III.56) \quad (Q^{**})^{iB} = -e^{-1}L_{es,zz}.$$

(The coefficients here defined are, of course, functions of the magnetic field).

One easily sees that the following local relations hold:

$$(III.57) \quad e^{-1}(Q^{**})_i^{iB} = TQ_i^i, \quad e^{-1}(Q^{**})_a^{iB} = TQ_a^i, \quad e^{-1}(Q^{**})^{iB} = TQ^{iB}.$$

These relations are, in a certain way, the «local» analoga of the «measurable» second relation of Thomson.

The Peltier coefficient is defined as the absorbed heat per unit flow of an electrical current across an isothermal junction from metal A to metal B . We can define two coefficients for the case of a transversal magnetic field: an isothermal Peltier coefficient: $(II_{AB})_i^{iB}$, with the conditions $i_y = 0$, $\partial T/\partial x = 0$, $\partial T/\partial y = 0$; an adiabatic Peltier coefficient: $(II_{AB})_a^{iB}$, with the conditions $i_u = 0$, $\partial T/\partial x = 0$, $J_{\bar{u},y} = 0$; and a coefficient for the case of a longitudinal magnetic field: $(II_{AB})^{iB}$, with the condition $\partial T/\partial z = 0$.

The evolution of heat at the junction between a metal A and a metal B can be found ⁽¹⁾ as the difference between the entropy flows before and after the junction, multiplied by the temperature T , since there is no entropy source at the surface separating the two metals. For the isothermal and adiabatic case in metal A inside the transversal magnetic field we have, from (III.12), (III.18) and (III.19),

$$(III.58) \quad T(J_{s,x})_i = (J_{\bar{u},x})_i + e^{-1}Ts_A i_x = (L_{se,xx} + e^{-1}Ts_A) i_x = e^{-1}\{(Q_A^{**})_i^{iB} + Ts_A\} i_x,$$

$$(III.59) \quad T(J_{s,x})_a = (J_{\bar{u},x})_a + e^{-1}Ts_A i_x = (L_{se,xx} + L_{ss,xy}L_{se,xy}/L_{ss,xx} + e^{-1}Ts_A) i_x = e^{-1}\{(Q_A^{**})_a^{iB} + Ts_A\} i_x.$$

From (III.12) and (III.20), for metal A inside a longitudinal magnetic field, we have

$$(III.60) \quad TJ_{s,z} = J_{\bar{u},z} + e^{-1}Ts_A i_z = (L_{se,zz} + e^{-1}Ts_A) i_z = e^{-1}\{(Q_A^{**})^{iB} + Ts_A\} i_z.$$

In the wire B we have ⁽¹⁾

$$(III.61) \quad TJ_{s,j} = e^{-1}(Q_B^{**} + Ts_B) i_j. \quad (j = 1, 2, 3)$$

The difference between (III.61) ($i = 1$) and (III.58), divided by the electric

current i_x gives

$$(III.62) \quad (H_{AB})_i^{iB} = e^{-1} \{ Q_B^{**} - (Q_A^{**})_i^{iB} + T(s_B - s_A) \} .$$

The difference between (III.61) ($i = 1$) and (III.59), divided by the electric current i_x gives

$$(III.63) \quad (H_{AB})_a^{iB} = e^{-1} \{ Q_B^{**} - (Q_A^{**})_a^{iB} + T(s_B - s_A) \} .$$

The difference between (III.61) ($i = 3$) and (III.60), divided by the electric current i_x gives

$$(III.64) \quad (H_{AB})^{iB} = e^{-1} \{ Q_B^{**} - (Q_A^{**})^{iB} + T(s_B - s_A) \} .$$

From (III.46), (III.57) and (III.62) one has

$$(III.65) \quad (H_{AB})_i^{iB} = -T\bar{Q}'_i ;$$

from (III.47), (III.57) and (III.63) one has

$$(III.66) \quad (H_{AB})_a^{iB} = -T\bar{Q}'_a ;$$

from (III.49), (III.57) and (III.64) one has

$$(III.67) \quad (H_{AB})^{iB} = -T\bar{Q}'^{iB} .$$

The coefficients \bar{Q}'_i , \bar{Q}'_a and \bar{Q}'^{iB} can properly be called « *thermoelectric power in a (transversal or longitudinal) magnetic field* »; hence it is correct to say that the relations (III.65), (III.66) and (III.67) are extensions of Thomson's second relation, to the system consisting of a metal subject to a magnetic field and a metal outside the magnetic field.

Remark. We should like to stress again the fact that, when the whole system is made of the same metal, the effects between the metal inside and outside the magnetic field can be studied. In such a case s_A indicates the specific entropy of electrons for the metal inside the field, (when the metal is isotropic it does not matter whether the field is transversal or longitudinal) and s_B indicates the specific entropy of electrons for the metal outside the magnetic field. As a matter of fact Onsager relations have been demonstrated, in chapter II, for a metal without magnetization or polarization. However, they can easily be extended to the present case, in which the influence of the induced field is negligible. As MAZUR and PRIGOGINE (*) have shown, the

local entropy production does not change, formally, when magnetization is also taken into account: the chemical potential μ only must be corrected with an additive term depending on the magnetic susceptibility of the metal and on the magnetic field. Since in our case both quantities are constant, the Onsager relations can be derived in the way outlined at the end of ⁽¹¹⁾.

Appendix on Tensor Notation.

We have used the Milne system of tensor notations ⁽²¹⁾ in this paper. The exterior product of an ordered pair of vectors \mathbf{a} , \mathbf{b} is a tensor

$$\mathbf{T} = \mathbf{a} \mathbf{b}, \text{ components: } T_{ik} = a_i b_k.$$

The divergence of a tensor and the gradient of a vector are written as

$$\text{Div } \mathbf{T}, \text{ components: } (\text{Div } \mathbf{T})_i = \sum_k (\partial/\partial x_k) T_{ki},$$

$$\text{Grad } \mathbf{a}, \text{ components: } (\text{Grad } \mathbf{a})_{ik} = (\partial/\partial x_i) a_k.$$

The interior product between a tensor and a vector is denoted by

$$\mathbf{T} \cdot \mathbf{a}, \text{ components: } (\mathbf{T} \cdot \mathbf{a})_i = \sum_k T_{ik} a_k,$$

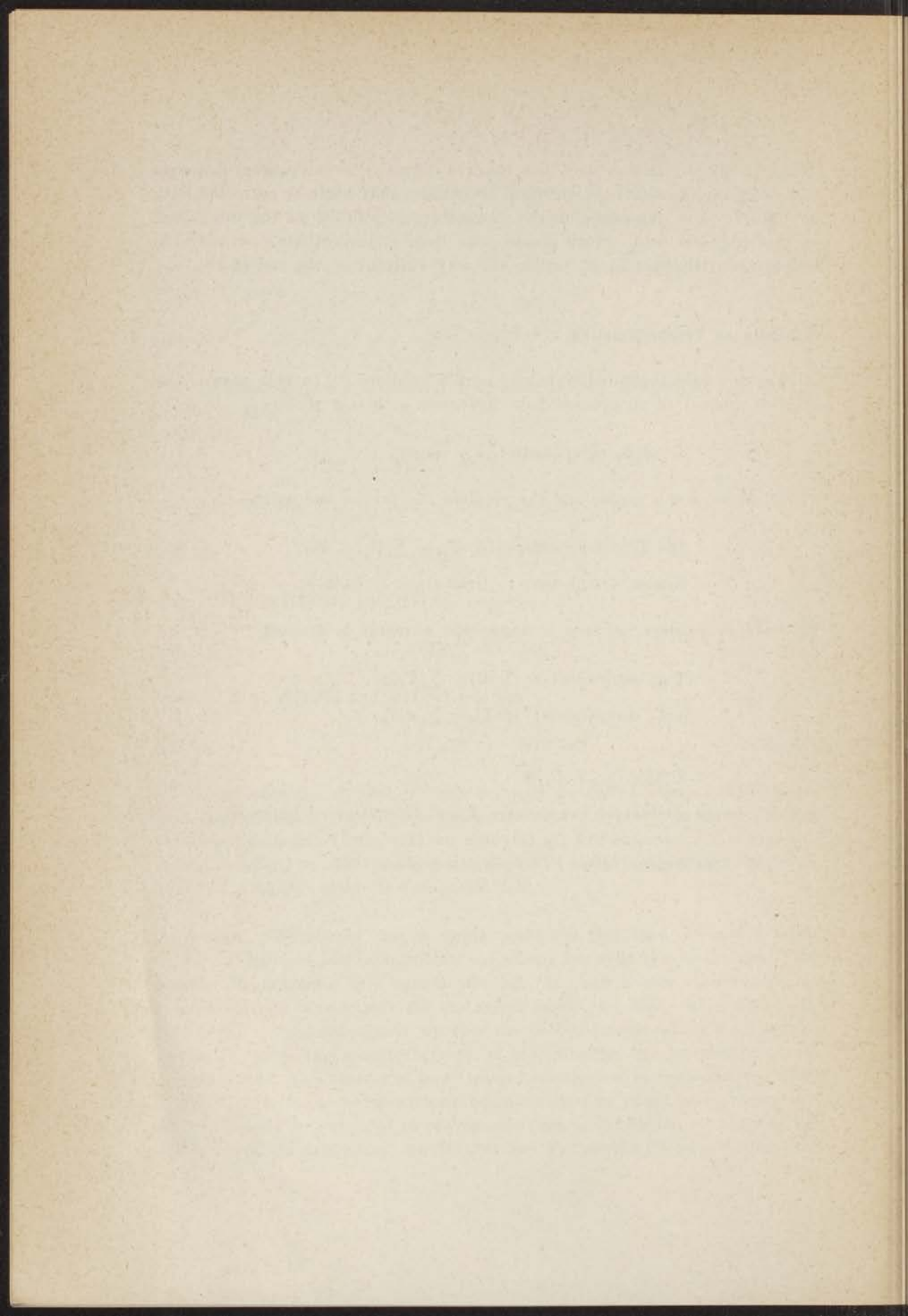
$$\mathbf{a} \cdot \mathbf{T}, \text{ components: } (\mathbf{a} \cdot \mathbf{T})_i = \sum_k a_k T_{ki}.$$

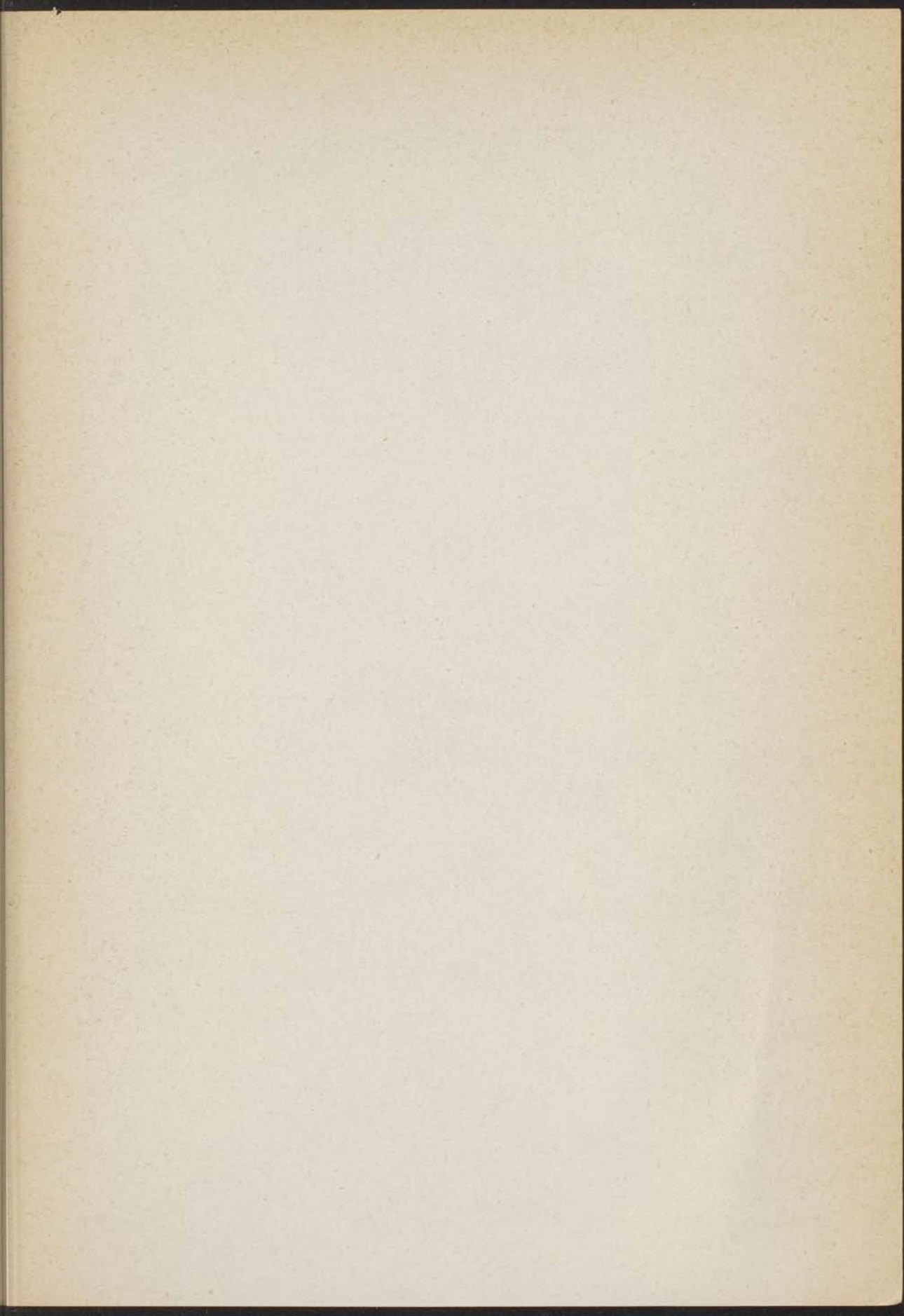
Finally

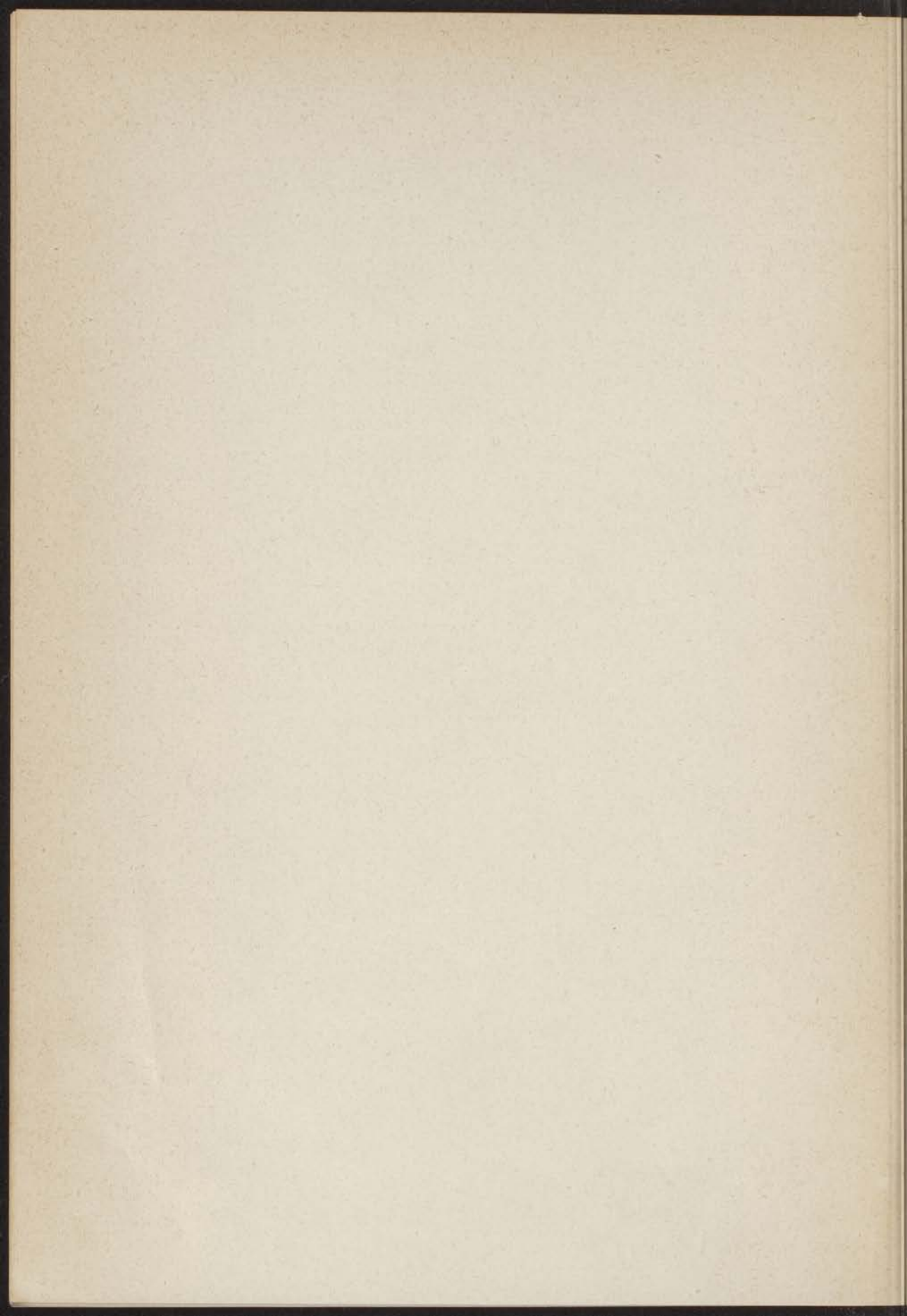
$$\mathbf{T} : \mathbf{U} = \sum_{i,k} T_{ik} U_{ki}$$

is the interior product of two tensors \mathbf{T} and \mathbf{U} contracted twice.

⁽²¹⁾ L. ROSENFELD: *Theory of Electrons* (Amsterdam, 1951).







STELLINGEN

I

Uit de vergelijking van de experimentele gegevens over de geografische breedte-effecten van de cosmische straling met de theoretische resultaten, die volgen uit het fenomenologische schema van CALDIROLA, blijkt de juistheid van genoemd schema.

P. CALDIROLA, R. FIESCHI en P. GULMANELLI: *Nuovo Cimento*, **9**, 5 (1952).

J. G. WILSON: *Progress in Cosmic Ray Physics* (North Holland Publishing Company, 1954), pp. 129-30.

II

De schema's van de elasticiteitscoëfficiënten van de tweede en derde orde, die Murnaghan geeft, zijn ten dele onjuist, zoals blijkt als men deze schema's als bijzondere gevallen van de betrokken algemene tensor uittekent.

FRANCIS D. MURNAGHAN: *Finite deformation of an elastic solid* (Wiley, 1951).

R. FIESCHI en F. G. FUMI: *Nuovo Cimento*, **10**, 865 (1953).

III

De tensoriële eigenschappen van kristallen worden dikwijls voorgesteld door grootheden, die geen tensoren zijn. Het verdient echter de voorkeur om tensorcoëfficiënten te gebruiken: met het voordeel van een uniformiteit in de definitie gaat dan samen een belangrijke vereenvoudiging in de afleiding van de coëfficiëntenschema's voor de verschillende symmetrieklassen.

F. G. FUMI en R. FIESCHI: Hoofdstuk over «*Point-group symmetry and the tensor properties of crystals*» in de «*International tables for crystallography*, vol. II: *Mathematical tables*». (Verschijnt binnenkort).

F. G. FUMI: *Acta Cryst.*, **5**, 44, 691 (1952).

IV

Proeven met gepolariseerd licht zouden kunnen uitmaken of het Z_2 -centrum (dat verantwoordelijk is voor een absorptieband, veroorzaakt door de aanwezigheid van tweewaardige kationen in kristallen van alkalihalogeniden) een vlak van symmetrie heeft, zoals Seitz heeft voorgesteld, of een sferische symmetrie, zoals Pick heeft voorgesteld. Indien het eerste geval zich voordoet zou het ook mogelijk zijn om vast te stellen of het vlak van het Z_2 -centrum evenwijdig is aan de kubusvlakken (100), zoals Seitz heeft voorgesteld, of evenwijdig aan de diagonaalvlakken (110). Voor het laatste zijn argumenten aan te voeren.

F. SEITZ: *Phys. Rev.*, **83**, 134 (1951).

M. UETA: *J. Phys. Soc. Japan*, **7**, 107 (1952).

V

De diffusie in roosters, zoals het cubisch gecentreerde van de bèta-fase van het systeem koper-zink, zou moeten verlopen volgens het mechanisme van het type cyclische diffusie of door paren roostergaten, indien men althans wil vasthouden aan het model van de diffusie van roostergaten.

VI

De discrepantie tussen de waarde van de vijfde viriaalcoëfficiënt van een gas van harde bollen, afgeleid uit de toestandsvergelijking en de waarde afgeleid uit de compressibiliteitsvergelijking, volgens de benaderingsmethode van Rushbrooke en Scoins voor de radiële distributiefunctie, toont dat deze benadering niet adequaat is.

B. R. A. NIJBOER en R. FIESCHI: *Physica*, **19**, 545 (1953).

VII

De fenomenologische relaties die Domenicali « postuleert » voor het verband tussen de entropiestroom, de deeltjes en de temperatuurgradiënt, om daarmee de thermoëlectrische verschijnselen in anisotrope media te behandelen, vallen onder het gebruikelijke schema van de thermodynamica der irreversibele processen.

CHARLES A. DOMENICALI: *Phys. Rev.*, **92**, 877 (1953).

VIII

De wederkerige relaties tussen onomkeerbare verschijnselen in anisotrope metalen, die verkregen zijn (dit proefschrift p. 40) als bijzondere gevallen van de relaties bewezen voor een mengsel van n elektrisch geladen componenten, kunnen ook direct bewezen worden.

R. FIESCHI, S. R. DE GROOT en P. MAZUR: *Physica*, **20**, 67 (1954).

IX

De relaties tussen de kruisverschijnselen van elektrische geleiding en warmtegeleiding (in magnetische velden) zijn (niet-trivale) voorbeelden van wederkerige relaties die volgen uit Casimir's formulering van de microscopische reversibiliteit met behulp van variabelen die even en oneven functies zijn van de deeltjessnelheden.

Dit proefschrift, formules (II.116) en (II.117).

X

Uit de wederkerige relaties tussen de coëfficiënten, die de galvanomagnetische en de thermomagnetische verschijnselen beschrijven, volgt dat de tweede relatie van THOMSON ook van toepassing is op een systeem dat bestaat uit een metaal binnen en een metaal buiten een magnetische veld.

Dit proefschrift, hoofdstuk II, § 6.

