

ON THE THEORY OF IRREVERSIBLE PROCESSES

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Table of Contents

Introduction	1
Summary	3
1 - Temporal Behavior of Statistical Ensembles	11
a - Behavior of Systems in Precisely Specified States	11
b - Behavior of Statistical Ensembles	15
2 - The Coarse-Grained Transition Matrix	18
3 - Special Properties of the Transition Matrix	21
a - No Magnetic Field	21
b - External Magnetic Field	24
4 - Form of the Transition Matrix for Small Times	27
5 - Time-Proportional Transition Probabilities	29
6 - The Condition of Equilibrium	34
a - The Principle of Equal A-Priori Probability of States	34
b - The Principle of Detailed Balancing	35
c - Resolution into Cycles	36
7 - Approach To The Equilibrium State	40
8 - The Principle of Dynamical Reversibility	48
9 - Onsager's Reciprocal Relations	49
a - Onsager's Derivation of the Reciprocal Relations	49
b - Alternative Derivation of the Onsager Relations	52

10 - The Production of Entropy and the Dissipation Function	59
a - The Dissipation Function	59
b - Dissipation Function in Absence of Magnetic Field	60
c - Dissipation Function in a Magnetic Field	63
11 - Steady-State Processes	69
a - The Method of Local Equilibrium	71
b - The Sommerfeld Free-Electron Theory, and Onsager's Relations	75
c - The Quasi-Thermodynamic Method of Kelvin	80
12 - Thermoelectric Effects	82
a - The Seebeck Effect	89
b - The Peltier Effect	91
c - The Thomson Effect	92
d - The Kelvin Relations	95
13 - The Thermo- and Galvanomagnetic Effects	96
a - The Isothermal Electrical Conductivity	100
b - The Adiabatic Electrical Conductivity	100
c - The Isothermal Heat Conductivity	101
d - The Adiabatic Heat Conductivity	101
e - The Isothermal Hall Effect	102
f - The Isothermal Nernst Effect	102
g - The Ettinghausen Effect	103
h - The Leduc-Righi Effect	103
i - The Bridgman Relation	104
Bibliography	106

Introduction

The methods of thermodynamics and of statistical mechanics have proved to be of great value in the understanding of the characteristics of systems in equilibrium. A comparably general method of treatment applicable to irreversible processes has, however, been lacking, although special methods of treatment have been developed for specific processes of interest. Such irreversible processes as the flow of electrical current, heat flow, chemical reaction, or diffusion are of the utmost practical importance and of great theoretical interest, and it would be clearly desirable to so extend the methods and scope of thermodynamics that it could form the basis for a satisfactory theory of irreversible processes.

The first notable progress in this direction was made by Onsager in the development of a very general and powerful set of Reciprocal Relations (cf. Onsager I and II; Casimir). These relations express a certain symmetry in the mutual interference of any two irreversible processes occurring simultaneously in a system.

The present work, devoted primarily to a discussion of Onsager's Relations, may properly be divided into two parts:

One part, forming the second half of this work, is concerned with the application of Onsager's Relations. The conditions of applicability are examined critically, and a detailed specific application is made to thermoelectric and to galvano- and thermomagnetic effects. The Kelvin Relations connecting the various thermoelectric coefficients, originally proposed by Kelvin on the basis of a "quasi-thermodynamic" argument, are a direct consequence of the Onsager Relations.

The first half of this work is concerned with a study of the fundamental principles on which the Onsager Relations are based. Although Onsager has given a very elegant derivation based on the time-symmetry of fluctuations in an ensemble, we have thought it worth while to develop an alternative derivation in which the details of the behavior of the ensemble are studied through an integration of the Schroedinger equation (cf. Tolman). The formalism involved in this derivation is also discussed with reference to the general question of the behavior of systems not in equilibrium.

At this point we wish to stress that it has not been our intention in this paper to investigate critically the ultimate fundamental principles upon which our treatment of irreversible processes is based. Rather, we have been content to adopt and extend an existing formalism (cf. Section 1). We feel, however, that this formalism requires additional critical investigation. In particular, the assumption of random phases in the ensemble (cf. Section 1, P. 16) plays a paramount role in the theory, but the justification of this assumption seems to us to be not completely satisfactory. This important question, and certain others of a similarly fundamental nature, has been glossed over in our present treatment, although we hope to pursue these questions further at a future time.

Summary

The purpose and scope of this work, as discussed in the introduction, are of a dual nature. The primary subject of interest is the Reciprocal Relations of Onsager. These relations are derived by an alternative method, and their application to steady-state processes (in particular, to thermoelectric effects) is discussed. As a secondary subject of interest the formalism dealing with the behavior in time of statistical ensembles is discussed with respect to the general question of the behavior of non-equilibrium systems. It therefore seems desirable to present here a summary by Sections which is so arranged that, after reading the Introduction and Summary, a reader interested in Onsager's Relations, or in thermoelectric effects alone, will be able to select and read only the appropriate Sections.

Sect. 1 - A theory of the behavior in time of a statistical ensemble has been developed (cf. Tolman) and forms the basis of this work. This theory applies a statistical averaging process to the result of an integration of the Schroedinger equation for the behavior of a single system. The fundamental assumption involved in the statistical averaging is the assumption of random phases. The result of this analysis may be summarized as follows. If \vec{W} is a "fine-grained probability vector" (or "fine-grained density vector"), the components of which give the probabilities of finding a system of the ensemble in the various eigenstates of some observable x , then

$$\vec{W}(t) = \{R\} \cdot \vec{W}(0) \quad (1-28)$$

where $\{R\}$, the "fine-grained transition matrix", has the properties

$$\sum_k R_{ik} = \sum_i R_{ik} = 1 \quad (1-29)$$

$$R_{ik} \geq 0 \quad (1-30)$$

$$\{R(-t)\} = \{R(t)\}^\dagger \quad (1-32)$$

The elements R_{ik} are known as explicit functions of the matrix elements of the Hamiltonian.

Sect. 2 - Although we thus have a formalism which allows us to predict the future fine-grained density vector in terms of the initial fine-grained density vector, it will be recognized that such a theory is not fully appropriate for the discussion of the behavior of practical macroscopic systems. This is so because our information on the initial state of the system is derived from measurements which are not, in general, sufficiently precise to distinguish among individual micro-states, and thus to give the fine-grained density vector. The lack of precision of the measurements of state leads to the definition of a "coarse-grained density vector", resulting from the averaging of fine-grained densities over groups of states of nearly equal properties. The future "coarse-grained density vector" $\vec{\rho}$ may be predicted in a similar fashion to the fine-grained density vector:

$$\vec{\rho}(t) = \{T\} \cdot \vec{\rho}(0) \quad (2-9)$$

where $\{T\}$ is a "coarse-grained transition matrix" with the properties

$$\sum_k T_{jk} = \sum_j T_{jk} = 1 \quad (2-10)$$

$$T_{jk} \geq 0 \quad (2-11)$$

$$\{T(-t)\} = \{T(t)\}^\dagger \quad (2-12)$$

Sect. 3 - Under certain special sets of conditions the transition matrix exhibits special symmetry properties in addition to the properties stated above. It is shown that

- a - The coarse-grained transition matrix is symmetric if
 - 1) There is no external magnetic field, and
 - 2) The variable of interest x (which provides us with the eigenstates which we use for a specification of the system) is an even function of the momenta of the particles composing the system.
- b - If the variable of interest x is an even function of the momenta, and of an externally applied magnetic field, then

$$\{T(A)\}^\dagger = \{T(-A)\} \quad (3-27)$$

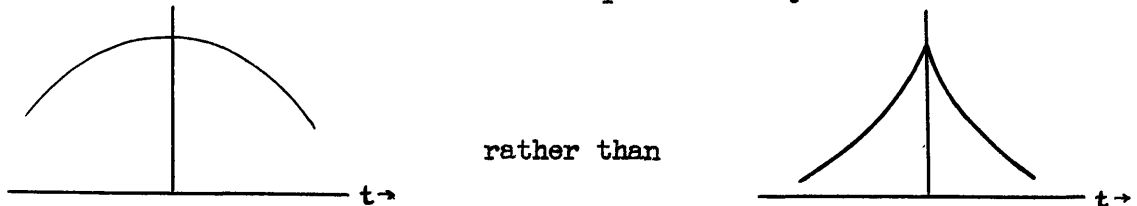
where A is the magnetic vector potential.

Sect. 4 - For small values of the time the transition matrix exhibits certain additional interesting properties. The behavior of the transition matrix elements for small times is considered, and it is shown that

- 1) The initial rate of change of any matrix element vanishes.
- 2) The elements T_{jk} and T_{kj} have the same initial value of the second derivative, so that there exists a short time interval in which the transition matrix is symmetric (See Figure in Section 4).

Sect. 5 - The coarse-grained transition matrix has a close formal similarity to the familiar matrix of time-proportional transition probabilities. Time-proportional transition-probabilities, however, have certain general properties which may be contrasted with the properties

of the coarse-grained transition elements. Thus, time-proportional transition elements are always symmetric, whereas the coarse-grained transition matrix is symmetric only under certain special conditions such as no external magnetic field. Furthermore, time-proportional transition probabilities do not have a vanishing initial rate of change, as do the coarse-grained transition elements. The derivation of the time-proportional transition probabilities shows, however, that they are valid only for small times. Thus the general symmetry is related to the symmetry which we have found for the coarse-grained transition elements for small times (see Section 4). On the other hand, there exists also a minimum time interval below which the time-proportional transition elements lose their validity, and this resolves the apparent discrepancy with respect to the initial rate of change. The vanishing of the initial rate of change of the transition elements requires that the most probable behavior of fluctuations curves for an equilibrium system shall be



as has been often mistakenly stated in the literature.

Sect. 6 - The characteristics of a system in equilibrium may be related to the properties of the transition matrix, as we have seen in the above discussion of fluctuations in equilibrium systems. In particular, the Principle of Equal A-Priori Probabilities of States, and the Principle of Detailed Balancing are immediate consequences of the form of the transition matrix. Detailed Balancing, however, is only valid in those special cases in which the transition matrix is symmetric.

In the more general case, the systems of the ensemble may be thought of as traversing closed cycles of states. If the magnetic field is reversed, these cycles of states are traversed in the reverse direction. A method of resolution of the transition matrix into such cycles is given and proved.

Sect. 7 - If an ensemble is established in some condition other than the equilibrium condition, it will eventually approach the condition of equilibrium. This approach to equilibrium, and the accompanying increase in entropy, are governed by the transition matrix, and the approach to equilibrium is studied in terms of the properties of the matrix.

Sect. 8 - As a final application of the transition matrix to the properties of systems, we consider the Principle of Dynamical Reversibility. This principle is of special interest to us here because it forms the basis of Onsager's derivation of the Reciprocal Relations. The Principle of Dynamical Reversibility takes a particularly simple form if the observable x is an even function of the momenta;

$$\bar{x}(t,A) = \bar{x}(-t,-A) \quad (8-1)$$

and this form of the principle follows immediately from our discussion in Section 3 of the transition matrix and of variables which are even in the momenta.

Sect. 9 - Having thus completed our discussion of the general properties of non-equilibrium systems, we turn our attention to the Reciprocal Relations of Onsager. These relations express a symmetry in the mutual interference of simultaneously occurring irreversible processes. The substance of Onsager's Relations is, briefly, as follows:

If two variables $x^{(1)}$ and $x^{(2)}$ are restrained to deviate from their equilibrium values, and if the restraint is lifted, then the subsequent rate of change of these variables is given by

$$\frac{\overline{\delta x}^{(1)}}{\delta t} = L_{11} \gamma^{(1)} + L_{12} \gamma^{(2)} \quad (9-24)$$

$$\frac{\overline{\delta x}^{(2)}}{\delta t} = L_{21} \gamma^{(1)} + L_{22} \gamma^{(2)}$$

where $\gamma^{(1)} = \frac{\delta S}{\overline{\delta x}^{(1)}}$, (9-28)

$$\gamma^{(2)} = \frac{\delta S}{\overline{\delta x}^{(2)}}$$

and $L_{12}(A) = L_{21}(-A)$ (9-30)

where A is the magnetic vector potential.

Onsager has derived the Reciprocal Relations by a consideration of the symmetry in time of the fluctuations in an ensemble, and this derivation is briefly reviewed. The validity of extending the macroscopic laws of irreversible processes to the regression of fluctuations, which underlies Onsager's derivation, has, however, been questioned (cf. Casimir). It seems desirable, therefore, to give an alternative derivation of the Reciprocal Relations which is based on the formalism of the coarse-grained transition matrix rather than on fluctuation theory.

Sect. 10 - The rate of production of entropy associated with an irreversible process may now be expressed as a quadratic function ("dissipation function") of the "currents". In the absence of a magnetic field the dissipation function plays the role of a potential, and the "forces" $\gamma^{(i)}$ are the derivatives of the dissipation function with respect

to the "currents" $\overline{\frac{\delta x^i}{\delta t}}$. In the presence of a magnetic field the currents may be considered as the sum of a dissipative part, which is an even function of the magnetic field, and of a non-dissipative part, which is an odd function of the magnetic field. The assumption of random phases among states in the ensemble leads to the impossibility of the flow of a non-dissipative current unaccompanied by a dissipative current.

In order that the entropy shall not ever spontaneously decrease, the kinetic coefficients L_{ij} must satisfy a certain inequality. This relation among the L_{ij} is a consequence of the properties of the transition matrix.

Sect. 11 - The application of Onsager's Relations to steady-state processes is now considered. In particular, the application to a system in which electric current and heat current flow simultaneously is studied, in preparation for our consideration of thermoelectric effects. It is seen that the application of the Reciprocal Relations to processes of this type involves a fundamental approximation. The nature of this approximation is studied by the free-electron theory of conductivity, and it is seen that the approximation is as valid as is the macroscopic law which governs the irreversible process (Ohm's Law). A consideration of the quasi-thermodynamic method of Lord Kelvin shows that this method is based on precisely the same approximation as is the application of Onsager's Relations, although the usual justification of Kelvin's argument, on the basis of "reversibility" of the thermoelectric effects, is of doubtful significance.

Sect. 12 - The application of Onsager's Relations to the study of thermoelectric effects gives a greater insight into the nature of these effects than does the analysis by Kelvin's quasi-thermodynamic method. A quantity which is of the nature of an entropy flow per particle plays a fundamental role in the theory of thermoelectric effects. The various effects are analyzed, and Kelvin's Relations among the effects are obtained.

Sect. 13 - The thermo- and galvanomagnetic effects may also be studied by the application of Onsager's Relations, and a relation, due to Bridgman, between the Nernst and Ettinghausen effects may be obtained.

1 - Temporal Behavior of Statistical Ensembles

In the equilibrium theory of statistical mechanics the properties of a system may be studied by an analysis of a statistical ensemble, the average properties of which correspond to the expectation values of the properties of the system. Similarly, the study of the properties of non-equilibrium systems may be based on the theory of the behavior in time of a statistical ensemble (cf. Tolman; Chapters 9-11). For the sake of unity and completeness we shall, in this section, give a brief resume of this theory, starting from fundamental principles and arriving at a description of the fine-grained density distribution in the ensemble.

a. Behavior of Systems in Precisely Specified States

Although our principal interest will be in the time behavior of a system the state of which is specified only macroscopically (i.e., in the time behavior of a statistical ensemble), we first consider the behavior of a system the state of which is specified with the optimum precision allowed by quantum mechanics. This study will provide the basis for the application of statistical reasoning and thus lead to information about ensembles.

If the Schroedinger wave-function for the system is ψ , and the Hamiltonian operator is \underline{H} , the Schroedinger equation for the time dependence of ψ is

$$\underline{H} \cdot \psi + \frac{\hbar}{2\pi i} \frac{\delta}{\delta t} \psi = 0 \quad (1-1)$$

We suppose that we are interested in some variable of the system (x) with the corresponding quantum mechanical operator \underline{x} . An

appropriate specification of the system will be in terms of the probability amplitudes $a_i(t)$ giving the distribution of ψ over the eigenfunctions ϕ_i of \underline{x} .

$$\psi(t) = \sum_i a_i(t) \phi_i \quad (1-2)$$

where $\underline{x} \phi_i = x_i \phi_i \quad (1-3)$

and $a_i(t) = \int \phi_i^* \psi d\tau \quad (1-4)$

Thus the Schroedinger equation becomes

$$\sum_i a_i(t) \underline{H} \phi_i + \frac{\hbar}{2\pi i} \sum_i \phi_i \frac{d}{dt} a_i(t) = 0 \quad (1-5)$$

Multiplying by ϕ_j^* and integrating, and recalling that the ϕ_i form an orthonormal set

$$\sum_i a_i(t) H_{ji} + \frac{\hbar}{2\pi i} \frac{d}{dt} a_j(t) = 0 \quad (1-6)$$

where the H_{ji} are the elements of the Hermitian matrix defined by

$$H_{ji} = \int \phi_j^* \underline{H} \phi_i d\tau \quad (1-7)$$

and where

$$H_{ji}^* = H_{ij} \quad (1-8)$$

By a repeated iteration of equation (1-6) we are able to evaluate all derivatives of $a_j(t)$. Thus, we have

$$\frac{da_j}{dt} = - \frac{2\pi i}{\hbar} \sum_i H_{ji} a_i \quad (1-9)$$

and

$$\begin{aligned} \frac{d^2 a_j}{dt^2} &= - \frac{2\pi i}{\hbar} \sum_i H_{ji} \frac{da_i}{dt} \\ &= - \frac{2\pi i}{\hbar} \sum_i H_{ji} \left[- \frac{2\pi i}{\hbar} \sum_k H_{ik} a_k \right] \\ &= + \left(\frac{2\pi i}{\hbar} \right)^2 \sum_k \left(\sum_i H_{ji} H_{ik} \right) a_k \\ &= + \left(\frac{2\pi i}{\hbar} \right)^2 \sum_k (H^2)_{jk} a_k \end{aligned} \quad (1-10)$$

where the last step follows from the rules of matrix multiplication.

By the process of mathematical induction we readily obtain, for the n th derivative

$$\frac{d^n a_j}{dt^n} = + \left(\frac{-2\pi i}{h} \right)^n \sum_k (H^n)_{jk} a_k \quad (1-11)$$

The probability amplitude at time t can now be expanded in terms of its value at time $t = 0$ by a Taylor's series in the time

$$\begin{aligned} a_j(t) &= a_j(0) + \frac{da_j(0)}{dt} \cdot t + \frac{1}{2!} \frac{d^2 a_j(0)}{dt^2} \cdot t^2 + \dots \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{2\pi i}{h} \right)^n \sum_k (H^n)_{jk} a_k(0) \cdot t^n \\ &= \sum_k \left[\sum_n \frac{1}{n!} \left(-\frac{2\pi i t}{h} \right)^n H^n \right]_{jk} a_k(0) \end{aligned}$$

which may be written symbolically as

$$a_j(t) = \sum_k \left[e^{-\frac{2\pi i}{h} H t} \right]_{jk} a_k(0) \quad (1-12)$$

or

$$a_j(t) = \sum_k U_{jk}(t) a_k(0) \quad (1-13)$$

where the operator \underline{U} is defined by

$$\underline{U}(t) = e^{-\frac{2\pi i}{h} \cdot \underline{H} t} \quad (1-14)$$

$$= \sum_n \frac{1}{n!} \left(-\frac{2\pi i t}{h} \right)^n \underline{H}^n \quad (1-15)$$

or

$$U_{ij}(t) = \sum_n \frac{1}{n!} \left(-\frac{2\pi i t}{h} \right)^n (H^n)_{ij} \quad (1-16)$$

To express the probability of finding the system in the i^{th} state at time t we recall that the probability W_i is related to the probability amplitude a_i by

$$W_i = a_i^* a_i \quad (1-17)$$

but, by (1-13)

$$a_i^* = \sum_m U_{im}^*(t) a_m^*(0) \quad (1-18)$$

whence

$$W_i(t) = \sum_{km} U_{im}^*(t) U_{ik}(t) a_m^*(0) a_k(0) \quad (1-19)$$

If we write the term for which $k = m$ explicitly we have

$$W_i(t) = \sum_k |U_{ik}|^2 W_k(0) + \sum'_{km} U_{im}^*(t) U_{ik}(t) a_m^*(0) a_k(0) \quad (1-20)$$

where the dash on the summation indicates that terms for which $m=k$ are to be omitted. This equation gives us our desired description of the behavior of systems in precisely specified states.

We shall be interested in the properties of the operator \underline{U} , and of the matrix $\{U\}$ with elements U_{jk} . We now see that the operator and matrix are unitary but not Hermitian:

By (1-15) we have

$$\underline{U}(-t) \underline{U}(t) = \underline{U}(0) = \underline{I} \quad (1-21)$$

where \underline{I} is the identity operator. Thus, for the matrix elements

$$\sum_k U_{ik}(-t) U_{kj}(t) = \delta_{ij} = \begin{cases} 1 & , i = j \\ 0 & , i \neq j \end{cases} \quad (1-22)$$

By (1-16) we also have

$$U_{ij}(t) = \sum_n \frac{1}{n!} \left(-\frac{2\pi i t}{h} \right)^n (H^n)_{ij}$$

whence

$$U_{ij}^*(t) = \sum_n \frac{1}{n!} \left(\frac{2\pi i t}{h} \right)^n (H^n)_{ij}^*$$

but by the Hermitian property (1-8) of \underline{H} we have

$$(H^n)_{ij}^* = (H^n)_{ji}$$

and

$$U_{ij}^*(t) = \sum_n \frac{1}{n!} \left(\frac{2\pi i t}{h} \right)^n (H^n)_{ji}$$

or

$$U_{ij}^*(t) = U_{ji}(-t) \quad (1-23)$$

We thus see that $\{U\}$ is not Hermitian. Combining (1-23) with (1-22)

we find

$$\sum_k U_{ki}^*(t) U_{kj}(t) = \delta_{ij} \quad (1-24)$$

and similarly

$$\sum_k U_{ik}^*(t) U_{jk}(t) = \delta_{ij} \quad (1-25)$$

We thus see that $\{U\}$ is unitary.

b. Behavior of Statistical Ensembles

A prediction of the future behavior of a system is provided by equation (1-20) if a precise specification of the initial state is known. We consider, however, the problem of predicting the future behavior of a system for which the original state is not so perfectly known. In particular, we consider that at $t = 0$ we know only the probability W_i of finding the system in each of the eigenstates ϕ_i of \underline{x} -

that is, we know the absolute magnitudes of all the probability amplitudes, but we have no information about the phase angles. A method of procedure is to adopt an ensemble composed of systems in every conceivable state consistent with the given information, giving equal a-priori probability to each such state; and to assume that the future behavior of the given system will be best predicted by the average behavior of the systems of the ensemble. This assumption is too familiar to warrant any discussion here - we adopt it forthwith and we shall, in the remainder of this work, deal with such ensembles. Accordingly, if the initial state of the system is given only in terms of the set of probabilities $W_i(0)$ then the future behavior will be obtained by averaging over all possible values of the phase angles of the probability amplitudes. In such an averaging process products such as $a_m^*(0) a_k(0)$ will vanish if $m \neq k$, and equation (1-20) becomes

$$W_i(t) = \sum_k |U_{ik}|^2 W_k(0) \quad (1-26)$$

It is now convenient to define a "fine-grained transition matrix" $\{R\}$, the matrix elements of which are defined by

$$R_{ik} \equiv |U_{ik}|^2 \quad (1-27)$$

Also, the quantities W_k ($k = 1, 2, \dots$) may be considered as the components of a "fine-grained probability vector" (or fine-grained density vector) \vec{W} .

Equation (1-26) may now be written in the form

$$\vec{W}(t) = \{R\} \cdot \vec{W}(0) \quad (1-28)$$

By equations (1-24) and (1-25) we see that $\{R\}$ has the important property

$$\sum_k R_{ik} = \sum_i R_{ik} = 1 \quad (1-29)$$

That is, the sum of the elements in any row or column of $\{R\}$ is unity.

In addition, from (1-27) we see that all the elements of $\{R\}$ are real and non-negative

$$R_{ik} \geq 0 \quad (1-30)$$

and by (1-23) we see that

$$R_{ik}(-t) = R_{ki}(t) \quad (1-31)$$

or
$$\{R(-t)\} = \{R(t)\}^\dagger \quad (1-32)$$

where \dagger indicates the adjoint matrix.

2 - The Coarse-Grained Transition Matrix

Although we have reviewed a formalism dealing with the temporal behavior of ensembles, it will be recognized that this formalism is not fully appropriate for the prediction of the behavior of systems in practice. The discrepancy arises from the fact that the formalism considers that our information about the system comes from measurements of such fine precision that it is possible to assign probabilities to individual states. Actually, any practical measurement on a complex system will not be able to distinguish among whole groups of states of nearly equal properties. It is this limit on the fineness of measurement which leads to the distinction between fine and coarse grain density (cf. Ehrenfest, p.60), a distinction which is fundamental to the concept of an entropy. Corresponding to this distinction between fine and coarse grain densities there is a distinction between fine and coarse grain transition matrices, and it is this distinction which we wish to develop in this section.

We recall first the relation between fine and coarse-grained densities. We consider that we have an ensemble of systems. If precise measurements were possible the probability of finding a system in the i^{th} state would be W_i . Consider, however, a group of μ states having properties so nearly equal that our measurements are incapable of distinguishing between them. Then the coarse-grained probability p_μ assigned to any state in the group is the average of the fine-grained probabilities of all the states in the group.

If at time $t = 0$ we make a measurement which yields as its result the probability of finding a system in the group of states μ then the appropriate ensemble which we choose to represent the system is one

which gives equal probability to each of the states in the group μ . Thus, immediately following a measurement, the fine-grained and coarse-grained densities in the representative ensemble are equal. As time progresses, however, inequalities appear between coarse and fine-grained densities because the values of the fine-grained transition matrix elements connecting various states within the group to some given state outside the group are not, in general, equal. However, because of the limit on the fineness of our subsequent measurements we shall not be able to detect these differences in fine-grained density among the states of a group. A matrix which predicts directly the coarse-grained probability at a later time may be easily obtained.

For convenience we temporarily make our notation more explicit. We shall label the eigenstates, not with a single index i , but with two indices. The Greek index ω or μ shall denote the group which contains the state. The arabic index l , m , n or p shall number the states within a given group. Thus l takes all values from unity to g_μ in the μ^{th} group.

The definition of the coarse-grained density may be written (cf. Pauli and Fierz, Equation 2)

$$\rho_{\mu m} = \frac{1}{g_\mu} \sum_{l=1}^{g_\mu} W_{\mu l} \quad (2-1)$$

and it is seen that $\rho_{\mu m}$ is independent of m , as, of course, it must be.

Consider that at time $t = 0$ we perform a measurement yielding us information in the form of coarse-grained densities. Then, in accordance with our remarks above, we adopt an ensemble in which the initial fine-grained and coarse-grained densities are equal. The fine-grained density at a later time is given, according to (1-28) by

$$W_{\mu 1}(t) = \sum_{\omega} \sum_{m} R_{\mu 1, \omega m}(t) \rho_{\omega m}(0) \quad (2-2)$$

$$= \sum_{\omega} \rho_{\omega m}(0) \sum_{m=1}^{\mathcal{E}_{\omega}} R_{\mu 1, \omega m}(t) \quad (2-3)$$

where we can remove $\rho_{\omega m}$ from the m-summation because it is independent of m. We may find $\rho_{\mu n}(t)$ by averaging as indicated in (2-1).

$$\rho_{\mu n}(t) = \frac{1}{\mathcal{E}_{\mu}} \sum_{\mu}^{\mathcal{E}_{\mu}} \left[\sum_{\omega} \rho_{\omega m}(0) \sum_{m=1}^{\mathcal{E}_{\omega}} R_{\mu 1, \omega m} \right] \quad (2-4)$$

which can be written as

$$\rho_{\mu n}(t) = \sum_{\omega} \sum_{p=1}^{\mathcal{E}_{\omega}} \rho_{\omega p}(0) \left[\frac{1}{\mathcal{E}_{\mu} \mathcal{E}_{\omega}} \sum_{\mu}^{\mathcal{E}_{\mu}} \sum_{m=1}^{\mathcal{E}_{\omega}} R_{\mu 1, \omega m} \right] \quad (2-5)$$

or

$$\rho_{\mu n}(t) = \sum_{\omega} \sum_p T_{\mu n, \omega p}(t) \rho_{\omega p}(0) \quad (2-6)$$

where

$$T_{\mu n, \omega p}(t) = \frac{1}{\mathcal{E}_{\mu} \mathcal{E}_{\omega}} \sum_{\mu}^{\mathcal{E}_{\mu}} \sum_{m=1}^{\mathcal{E}_{\omega}} R_{\mu 1, \omega m} \quad (2-7)$$

Thus $T_{\mu n, \omega p}$ is just the average of the fine-grained transition matrix elements over the states in the two groups. In terms of our old, less explicit, notation we can write

$$\rho_i(t) = \sum_j T_{ij}(t) \rho_j(0) \quad (2-8)$$

or
$$\vec{\rho}(t) = \{T(t)\} \cdot \vec{\rho}(0) \quad (2-9)$$

It is clear that from the characteristics (1-29), (1-30), and (1-32) of the fine-grained transition matrix $\{R\}$ we may also write for the coarse-grained transition matrix $\{T\}$:

$$\sum_k T_{ik} = \sum_i T_{ik} = 1 \quad (2-10)$$

$$T_{ik} \geq 0 \quad (2-11)$$

$$\{T(-t)\} = \{T(t)\}^T \quad (2-12)$$

3 - Special Properties of the Transition Matrix

Under completely general conditions the transition matrix is subject only to the restrictions (2-10), (2-11) and (2-12). Under special conditions, however, the transition matrix exhibits more stringent symmetry relations. Thus, it is well-known, and may be easily shown, that if the variable of interest x (which provides us with the eigenstates used for a specification of the system) is the energy, then the fine-grained transition matrix reduces to the identity matrix. This is the quantum mechanical analogue of the classical principle of conservation of energy, for it requires that any distribution over the energy eigenstates shall be constant in time. We consider in this section two further sets of special conditions which lead to special properties of the transition matrix.

a. No Magnetic Field

We now show that the transition matrix is symmetric if the system satisfies two requirements:

- 1) No external magnetic or Coriolis fields shall be present.
- 2) The variable of interest x (which provides us with the eigenfunctions and eigenstates which we use for a specification of the system) shall classically be an even function of the momenta of the particles composing the system.

The quantum mechanical formulation of these two requirements is that \underline{H} and \underline{x} should be real operators. That is

$$1) \quad \underline{H}^* = \underline{H} \quad (3-1)$$

$$2) \quad \underline{x}^* = \underline{x} \quad (3-2)$$

In order to demonstrate the symmetry of $\{T\}$ we first note that the reality of \underline{x} imposes a restriction on the form of the eigenfunctions ϕ_k . For by definition

$$\underline{x} \phi_k = x_k \phi_k \quad (3-3)$$

where x_k is a real constant. Taking complex conjugates, and using the reality of \underline{x} ,

$$\underline{x} \phi_k^* = x_k \phi_k^*$$

so that ϕ_k^* is also an eigenfunction of \underline{x} corresponding to the eigenvalue x_k . Then if x_k is not degenerate

$$\phi_k^* = \text{constant} \cdot \phi_k \quad (3-4)$$

If x_k is degenerate then it is possible to choose the ϕ_k in such a way as to make (3-4) true, and we shall assume that this has been done.

Because of the normalization of the eigenfunctions the constant in equation (3-4) must have the modulus unity. We thus write

$$\phi_k = |\phi_k| e^{i\delta_k} \quad (3-5)$$

This form of the eigenfunctions, and the reality of \underline{H} , now imposes a restriction on the matrix elements of powers of \underline{H} . For consider

$$\begin{aligned} (H^n)_{jk} &= \int \phi_j^* \underline{H}^n \phi_k \, d\tau \\ &= e^{i(\delta_k - \delta_j)} \int |\phi_j| \underline{H}^n |\phi_k| \, d\tau \end{aligned}$$

and because of the reality of \underline{H} the integral is a real function. Thus

$$(H^n)_{jk} = \pm e^{i(\delta_k - \delta_j)} |(H^n)_{jk}| \quad (3-6)$$

Also, because \underline{H} is Hermitian we have

$$(\underline{H}^n)_{jk}^* = (\underline{H}^n)_{kj} \quad (3-7)$$

whence
$$|(\underline{H}^n)_{jk}| = |(\underline{H}^n)_{kj}| \quad (3-8)$$

Now, by equation (1-16):

$$\begin{aligned} U_{jk} &= \sum_n \frac{1}{n!} \left(\frac{-2\pi i t}{h} \right)^n (\underline{H}^n)_{jk} \\ &= e^{i(\delta_k - \delta_j)} \sum_n \frac{1}{n!} \left(\frac{-2\pi i t}{h} \right)^n (\pm 1) |(\underline{H}^n)_{jk}| \quad (3-9) \end{aligned}$$

and by (3-8) we see that the summation is a symmetric function of the indices j and k . Thus it follows that $R_{jk} \equiv U_{jk}^* U_{jk}$ is also a symmetric function of the indices, or

$$R_{jk} = R_{kj} \quad (3-10)$$

which may be written in the more explicit notation of Section 2 as

$$R_{\mu 1, \omega m} = R_{\omega m, \mu 1} \quad (3-11)$$

If we sum over l and m , and divide by $g_\mu g_\omega$ we immediately obtain, by

(2-7)

$$T_{\mu n, \omega p} = T_{\omega p, \mu n} \quad (3-12)$$

or
$$\{T\} = \{T\}^\dagger \quad (3-13)$$

Thus we have proved the symmetry of the coarse-grained transition matrix under the conditions (3-1) and (3-2).

b. External Magnetic Field

We now show that if the variable x is classically an even function of the particle momenta and of an externally applied magnetic field, then

$$T_{jk}(A) = T_{kj}(-A) \quad (3-14)$$

where A is the magnetic vector potential.

As above, we have

$$\underline{x}^* = \underline{x} \quad (3-15)$$

However \underline{H} is no longer a real operator in the presence of an external magnetic field, but

$$\underline{H}^*(A) = \underline{H}(-A)$$

This may be easily seen if we neglect spin, for the Hamiltonian will involve the magnetic field only through constructs of the form

$$\sum_n (p_n - \frac{e}{c} A_n)^2$$

where n is an index which numbers the various particles, p_n is the momentum of the n^{th} particle, and A_n is the magnetic vector potential acting on the n^{th} particle. The magnetic vector potential is composed of the externally applied potential A , and of the potential produced by the motion of the other charged particles. Thus the Hamiltonian involves constructs of the form

$$\sum_n (p_n + \text{constant} \cdot \sum_m p_m - \frac{e}{c} A)^2$$

and, after replacing the momenta by the operators $\frac{h}{2\pi i} \frac{\delta}{\delta q_n}$, we see that the Hamiltonian operator satisfies the condition

$$\underline{H}^*(A) = \underline{H}(-A) \quad (3-16)$$

Now, subject to the two conditions (3-15) and (3-16), we may follow a logic similar to that of part (a) above, and thus arrive at (3-14):

Again the eigenfunctions have the form (3-5), and are even functions of the magnetic field.

$$\phi_k = |\phi_k| e^{i\delta_k} \quad (3-17)$$

The matrix elements of powers of \underline{H} are now

$$(\underline{H}^n(A))_{jk} = e^{i(\delta_k - \delta_j)} \int |\phi_j| \underline{H}^n(A) |\phi_k| d\tau \quad (3-18)$$

and because \underline{H} is Hermitian we can write this as

$$(\underline{H}^n(A))_{jk} = e^{i(\delta_k - \delta_j)} \int |\phi_k| \underline{H}^{n*}(A) |\phi_j| d\tau$$

or, by (3-16)

$$(\underline{H}^n(A))_{jk} = e^{i(\delta_k - \delta_j)} \int |\phi_k| \underline{H}^n(-A) |\phi_j| d\tau \quad (3-19)$$

Comparing (3-18) and (3-19) we see that we can write

$$(\underline{H}^n(A))_{jk} = e^{i(\delta_k - \delta_j)} \mathcal{H}_{jk}^n(A) \quad (3-20)$$

where

$$\mathcal{H}_{jk}^n(A) = \mathcal{H}_{kj}^n(-A) \quad (3-21)$$

Then, by equation (1-16)

$$U_{jk}(A) = e^{i(\delta_k - \delta_j)} \sum_n \frac{1}{n!} \left(\frac{-2\pi i t}{h} \right)^n \mathcal{H}_{jk}^n(A) \quad (3-22)$$

and in accordance with the symmetry property (3-21) we see that we can write

$$U_{jk}(A) = e^{i(\delta_k - \delta_j)} \mathcal{U}_{jk}(A) \quad (3-23)$$

where
$$\mathcal{U}_{jk}(A) = \mathcal{U}_{kj}(-A) \quad (3-24)$$

Now, by (1-27)

$$\begin{aligned} R_{jk}(A) &= U_{jk}^*(A) U_{jk}(A) \\ &= \mathcal{U}_{jk}^*(A) \mathcal{U}_{jk}(A) \end{aligned}$$

whence
$$R_{jk}(A) = R_{kj}(-A) \quad (3-25)$$

and finally by (2-7)

$$T_{jk}(A) = T_{kj}(-A) \quad (3-26)$$

or
$$\{T(A)\} = \{T(-A)\}^\dagger \quad (3-27)$$

which is the property we have sought to prove.

4 - Form of the Transition Matrix for Small Times

The transition matrix exhibits, for small values of the time t , certain interesting properties which we shall develop in this section.

We recall first that the transition matrix has the following general properties

$$\sum_k T_{jk} = \sum_j T_{jk} = 1 \quad (4-1)$$

$$T_{jk} \geq 0 \quad (4-2)$$

$$T_{jk}(-t) = T_{kj}(t) \quad (4-3)$$

Consider now the expansion of the matrix elements in a Taylor's series in the time

$$T_{jk}(t) = T_{jk}^{(0)} + T_{jk}^{(1)} \cdot t + T_{jk}^{(2)} \cdot t^2 + \dots + T_{jk}^{(n)} \cdot t^n + \dots \quad (4-4)$$

where the $T_{jk}^{(n)}$ are constants. But we have $\{T(0)\} = \{I\}$, the identity matrix. Thus

$$T_{jk}^{(0)} = \delta_{jk} \quad (4-5)$$

and for the non-diagonal elements

$$T_{jk}(t) = T_{jk}^{(1)} \cdot t + T_{jk}^{(2)} \cdot t^2 + \dots \quad j \neq k \quad (4-6)$$

Then, by (4-3)

$$T_{kj}(t) = -T_{jk}^{(1)} \cdot t + T_{jk}^{(2)} \cdot t^2 + \dots + (-1)^n T_{jk}^{(n)} \cdot t^n + \dots \quad (4-7)$$

so that

$$T_{kj}^{(n)} = (-1)^n T_{jk}^{(n)} \quad (4-8)$$

If we now consider times so small that all powers of t higher than the first can be neglected, then

$$T_{jk}(t) = T_{jk}^{(1)} \cdot t \quad \text{and} \quad T_{kj}(t) = -T_{jk}^{(1)} \cdot t$$

and by (4-2) both of these must be non-negative. We are thus forced to the conclusion

$$T_{jk}^{(1)} = 0, \quad j \neq k \quad (4-9)$$

and the smallest non-zero term in (4-6) and (4-7) is the term in t^2 .

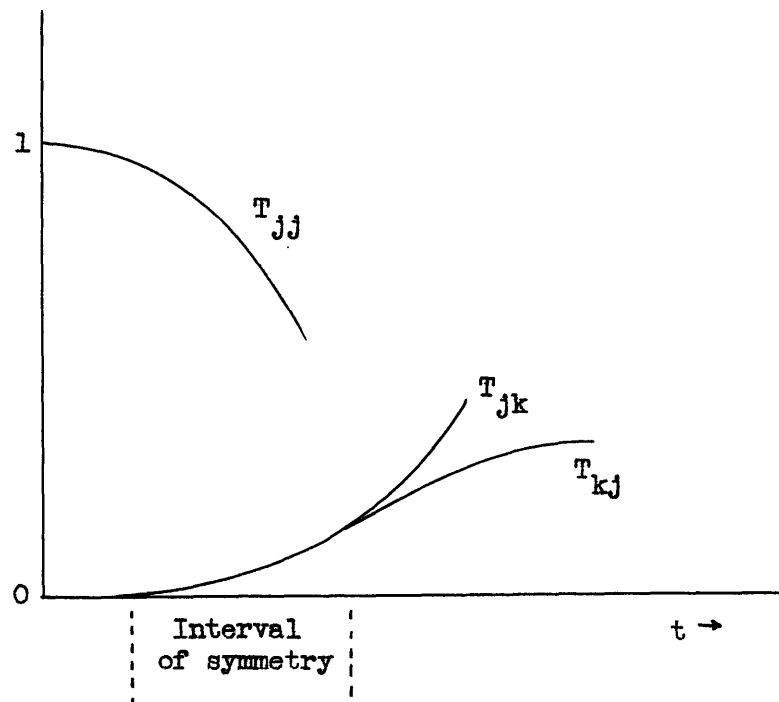
Considering times so small that all higher powers of t can be neglected we have

$$T_{jk}(t) = T_{jk}^{(2)} \cdot t^2 \quad \text{and} \quad T_{kj}(t) = T_{kj}^{(2)} \cdot t^2$$

so that

$$T_{jk}(t) = T_{kj}(t) \quad t \ll \left| \frac{T_{jk}^{(2)}}{T_{jk}^{(3)}} \right| \quad (4-10)$$

If we plot the transition matrix elements against time we obtain a graph of the following form. The initial slope of both T_{jk} and T_{kj} is zero by (4-9). The initial curvatures are identical by (4-10) - thus giving an interval of symmetry.



5 - Time Proportional Transition Probabilities

The coarse-grained transition matrix exhibits a close formal similarity to the familiar matrix of time-proportional transition probabilities. Because of this formal similarity, and because the application of time-proportional transition probabilities is so conceptually simple, it is interesting to consider the relationship between these two matrices. In particular, we shall compare the simple linear time dependence of the time-proportional transitions with the more complicated time dependence of the coarse-grained transition elements; and we shall compare the general symmetry of the time-proportional transitions with the less stringent symmetry properties of the coarse-grained transition elements.

Time-proportional transition probabilities arise in quantum mechanics in the following way (cf. Pauli). Consider the true Hamiltonian of the system to be decomposed into two terms - the "unperturbed Hamiltonian" and a "perturbation operator" - the latter being chosen to be small. The eigenstates among which the system will be considered to be undergoing transitions are chosen to be the eigenstates of the unperturbed Hamiltonian. If the wave-function of the system is expanded in terms of these eigenfunctions, then the time dependence of the probability amplitudes follows directly from the time-dependent Schroedinger equation. One obtains, thereby, a set of simultaneous first-order differential equations of the form

$$\frac{d}{dt} c_j = \frac{-2\pi i}{h} \sum_k v_{jk} e^{\frac{2\pi i t}{h} (E_j^0 - E_k^0)} c_k, \quad (5-1)$$

j=1,2....

the c_k 's being defined by

$$\psi = \sum_k c_k e^{\frac{-2\pi i}{h} E_k^0 t} \phi_k$$

where

V_{jk} is the matrix element of the perturbation operator

E_k^0 is the eigenvalue of the unperturbed Hamiltonian
in the k^{th} eigenstate

ϕ_k is the k^{th} eigenfunction of the unperturbed
Hamiltonian.

For small time intervals an approximate integration of these equations is effected by merely replacing the values of the c_k appearing on the right side of (5-1) by their initial values, and integrating. If the system is originally in the state k this procedure leads to the probability of finding it, after a short time interval, in the state j :

$$W_j(t) = 4 |V_{jk}|^2 \cdot \frac{\sin^2 \frac{\pi}{h}(E_j^0 - E_k^0) \cdot t}{(E_j^0 - E_k^0)^2} \quad (5-2)$$

It is customary at this point to make the assumption that in small energy ranges including the states j and k there are many states, and to average (5-2) over these groups of states (cf. Tolman, p. 431). Because of the form of (5-2) this averaging over energy intervals results in an expression which is linear in the time. The result of this procedure may be summed up in the relations:

$$\vec{\rho}(t) = \{P\} \cdot \vec{\rho}(0) \quad (5-3)$$

where

ρ_j is the average of W_j over a group of states surrounding j , i.e., ρ_j is the coarse-grained density.

$$P_{jk} = P_{kj} \quad (5-4)$$

$$P_{jk} = \delta_{jk} + P_{jk} \cdot t \quad (5-5)$$

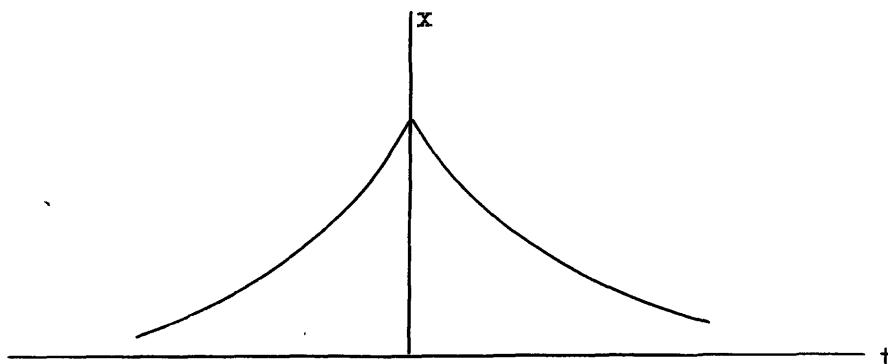
$$\sum_j P_{jk} = \sum_k P_{jk} = 1 \quad (5-6)$$

The symmetry of $\{P\}$ follows from the Hermitian property of the perturbation operator, whereby $|V_{jk}|^2 = |V_{kj}|^2$ in (5-2).

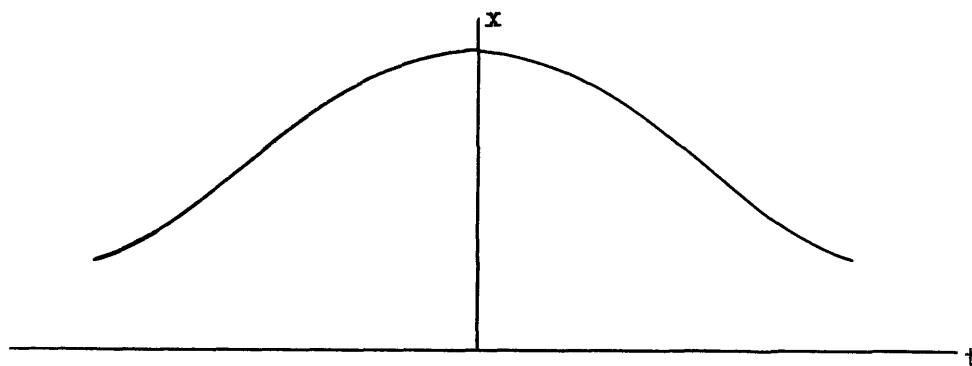
It should be noted that although the validity of (5-3) is limited to small time intervals, there exists also a lower bound to the time interval, below which (5-3) again loses its validity. We must have

$$t > \frac{h}{2\pi\Delta E} \quad (5-7)$$

where ΔE is the range of energies of the states in a group. For if we consider times less than $\frac{h}{2\pi\Delta E}$ then the Heisenberg uncertainty relation will cause the uncertainty in energy to be so large as to prevent us from distinguishing between different groups of states - which we have assumed that we are capable of doing. This lower bound on t is very important, for it resolves the apparent paradox which arises from the demonstration in Section 4 that the initial slope of the coarse-grained transition elements vanishes, whereas the time-proportional transition elements have a linear time dependence. This discrepancy has been the source of frequent confusion in the literature - particularly in regard to the discussion of the shape of fluctuation curves. It has been often stated that if some variable of a system in equilibrium is plotted against time, and if at $t = 0$ this variable is observed to deviate from its equilibrium value, then the average behavior of the variable in time will be as shown.



A non-zero initial rate of change is attributed to x - this being expected by (5-5) if the restriction (5-7) is not properly appreciated. Actually, it follows from (4-9) that the average behavior of the variable will be such as to show no initial rate of change:



We now turn to a brief comparison of the symmetry properties of the time-proportional transition probabilities and of the coarse-grained transition elements. According to (5-4) the time-proportional transition matrix $\{P\}$ is always symmetric, whereas $\{T\}$ in general is not. The only special features of $\{P\}$ are that it is based on eigenstates of a Hamiltonian operator, and that it is an approximation for small times. However no unique symmetry properties of a Hamiltonian operator are used in the derivation of $\{P\}$, and the symmetry must be a result of the limitation to small times. The source of this symmetry is made clear by the considerations of Section 4 - the symmetry being

precisely that which is shown for small times in the figure of Section 4.

It should, finally, be noted that the applicability of time-proportional transition probabilities is more restricted than is that of the coarse-grained transition matrix. This arises from the fact that time-proportional transitions apply only to transitions between eigenstates of a Hamiltonian, and are thus suited only to a description of the temporal behavior of variables which commute with this unperturbed Hamiltonian. Only for such variables is it possible to choose a set of states which are simultaneous eigenstates of the variable and of the unperturbed Hamiltonian. As an illustration of this restriction we may consider the second special case of Section 3 - in which the operator \underline{x} is real, but the true Hamiltonian operator is not. In order that \underline{x} and the unperturbed Hamiltonian may have simultaneous eigenfunctions it is necessary (but not sufficient) that the unperturbed Hamiltonian be real. This requires that all terms in the true Hamiltonian containing odd powers of the magnetic field must be assigned to the perturbation operator, and since the perturbation operator must be small, we are thus restricted to small values of the magnetic field. In addition, the reality of the unperturbed Hamiltonian severely limits the type of eigenstates which we can consider.

6 - The Condition of Equilibrium

The form of the coarse-grained transition matrix has certain consequences in respect to the nature of the equilibrium state. Although the consequences which we shall consider in this section are well-known we consider them here principally in order to explicitly show their relation to the properties of the transition matrix.

After disposing briefly of the rather trivial principle of the equal a-priori probabilities of states we shall be chiefly interested in the Principle of Detailed Balancing. This latter principle, which states that the transitions $j \rightarrow k$ and $k \rightarrow j$ occur with equal frequency in the ensemble, is valid only under those special conditions in which $\{T\}$ is symmetric. In the more general case we shall show that the systems of the ensemble may be thought of as describing closed cycles among groups of states, and the transition matrix will be resolved into such cycles.

a - The Principle of Equal A-Priori Probability of States may be expressed by the statement that if

\vec{I} = the vector with all components unity

N = the number of states

then the density vector

$$\vec{\rho} = \frac{1}{N} \vec{I} \quad (6-1)$$

remains constant in time. That this is true follows from

$$\vec{\rho}(t) = \{T\} \cdot \vec{\rho}(0)$$

and

$$\sum_k T_{jk} = 1$$

so that
$$\{T\} \cdot \frac{1}{N} \vec{I} = \frac{1}{N} \vec{I}$$

Thus the condition of random phases and of equal population of all the states in the ensemble is a condition of equilibrium.

b - The Principle of Detailed Balancing

Because all states in the ensemble are equally populated in equilibrium we see that the number of systems which undergo the transition $k \rightarrow j$ in a time t is proportional to the transition element $T_{jk}(t)$. Thus symmetry of $\{T(t)\}$ implies that the transitions $j \rightarrow k$ and $k \rightarrow j$ occur with equal frequency in the ensemble, and this is the content of the Principle of Detailed Balancing. This principle is valid only under those special conditions in which $\{T\}$ is symmetric - such as the condition of no external magnetic field and eigenstates of a variable which is even in the momenta (see Special Case a of Section 3); or for short time intervals (see Section 4). In the more general case, such as that involving a magnetic field (see Special Case b of Section 3), we do not have detailed balancing. We shall show that in the general case the transition elements may be grouped into closed cycles, so that the systems of the ensemble may be thought of as continuously traversing such cycles of states. It seems conceivable that the passage of a system through such cycles of states may give rise to observable effects, but we may expect to be able to observe only cycles involving three or more states - for detailed balancing may be expected to lead to a cancellation of the effects of individual transitions and their inverses.

c - Resolution into Cycles

Preparatory to proving that the transition elements can be grouped into closed cycles, we shall first give a recipe for accomplishing the resolution. We shall then prove that the recipe does, in fact, accomplish the resolution required.

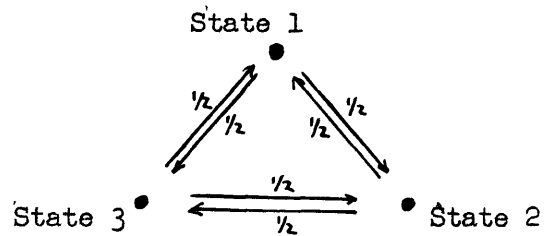
We shall designate a collection of n equal transition elements, which carry a system through n separate states and thence back to the initial state, by the term "n-fold cycle".

$$T_{kj} T_{lk} T_{ml} \cdot \cdot \cdot T_{sr} T_{qs} T_{jq}$$

The matrix with these elements as matrix elements, and with all other elements zero, we shall term an "n-fold cyclic matrix".

It should be noted that the resolution into cyclic matrices is not unique. As an illustration of this consider the following matrix, which satisfies all the conditions of a transition matrix

$$\begin{pmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{pmatrix}$$



This matrix can be resolved into the sum of three 2-fold cyclic matrices:

$$\begin{pmatrix} 0 & 1/2 & 0 \\ 1/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 1/2 \\ 0 & 0 & 0 \\ 1/2 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1/2 \\ 0 & 1/2 & 0 \end{pmatrix}$$

The matrix may alternatively be resolved into the sum of two 3-fold cyclic matrices:

$$\begin{pmatrix} 0 & 1/2 & 0 \\ 0 & 0 & 1/2 \\ 1/2 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 1/2 \\ 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \end{pmatrix}$$

The diagram illustrates two 3-fold cyclic matrices. The left matrix is represented by a triangle with three nodes (states 1, 2, 3) and three directed edges, each labeled with a probability of 1/2. The edges are: 2 → 1, 3 → 2, and 1 → 3. The right matrix is represented by a similar triangle with three nodes and three directed edges, each labeled with a probability of 1/2. The edges are: 1 → 3, 3 → 1, and 2 → 1.

In order to remove this indefiniteness we shall agree to give small cycles priority over larger cycles in our resolution of a transition matrix.

Our procedure for the resolution of a transition matrix is, then, as follows:

First, form the N 1-fold cyclic matrices each of which contains as its only non-zero element one of the N diagonal elements of the given transition matrix. Subtract these N 1-fold matrices from the given transition matrix.

Second, choose the smaller of the two elements T_{12} and T_{21} in the remaining matrix, and with this element form a 2-fold matrix connecting the states 1 and 2. Subtract this matrix from the remainder of the transition matrix, and repeat the process for states 1 and 3. Proceed in this way until all combinations of two states are exhausted. (If the original transition matrix is symmetric this completes the resolution.)

Third, choose the smallest of the three elements T_{12} , T_{23} , T_{31} in the remainder of the transition matrix, and with this element form a 3-fold cyclic matrix connecting the states 1, 2, and 3. Subtract

this 3-fold matrix from the remainder of the transition matrix. Repeat for the permutation T_{21} , T_{13} , T_{32} and, in turn, for all possible permutations of three states.

Continue in this way for permutations of four states, five states ... and finally for N states.

When this final N -fold cyclic matrix is subtracted the remainder will be a matrix with no non-zero elements. That this is so will now be proven:

To prove that our recipe given above really does accomplish the resolution of any transition matrix into the sum of cyclic matrices we first note the following property. According to (2-10) the sum of the elements in the k^{th} row of a transition matrix is equal to the sum of the elements in the k^{th} column. Furthermore, any cyclic matrix has this property, as does any matrix obtained by subtracting cyclic matrices from a transition matrix. Thus, we may conclude that in any matrix obtained by subtracting cyclic matrices from a transition matrix the existence of a non-zero element in the k^{th} row implies the existence of a non-zero element in the k^{th} column.

Consider now that after carrying out our recipe above we are left with a matrix with at least one non-zero element - say T_{ij} . We must have $i \neq j$ because we have assumed that all 1-fold cyclic matrices have been subtracted. Then, by the paragraph above, there exists an element T_{ki} such that $k \neq i$ because we have assumed the subtraction of all 1-fold cyclic matrices, and $k \neq j$ because we have assumed the subtraction of all 2-fold cyclic matrices. We indicate all of this symbolically by

Assume $\exists T_{ij} \neq 0 \exists i \neq j$ (1-fold)

$\therefore \exists T_{ki} \neq 0 \exists k \neq i$ (1-fold), $k \neq j$ (2-fold)

and we may continue

$\therefore \exists T_{pk} \neq 0 \exists p \neq k$ (1-fold), $p \neq i$ (2-fold), $p \neq j$ (3-fold)

$\therefore \exists T_{mp} \neq 0 \exists m \neq p$ (1-fold), $m \neq k$ (2-fold), $m \neq i$ (3-fold), $m \neq j$ (4-fold)

$\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots$

$\therefore \exists T_{rq} \neq 0 \exists r \neq q$ (1-fold), ..., $r \neq i$ (n-1)-fold, $r \neq j$ (n-fold)

which requires that there exist $(n + 1)$ integers (r, q, \dots, i, j) all $\leq n$ and all different. This is, of course, impossible. Thus, after carrying out our recipe we could not be left with a matrix containing any non-zero elements. We have thus proved that any transition matrix can, by our given recipe, be resolved into the sum of cyclic matrices.

It may be noted that the adjoint of any cyclic matrix corresponds to the system traversing the cycle of states in the reverse order. But by (3-27) the reversal of the magnetic field is equivalent to taking the adjoint of the transition matrix. Thus, if the magnetic field is reversed, the system may be thought of as traversing all the cycles of states in the reverse direction.

7 - Approach to the Equilibrium State*

We have seen in the preceding section that the condition of random phases and equal population of all states corresponds to a condition of equilibrium. In this section we shall be concerned with the question of whether an ensemble set up in accordance with some arbitrary density vector will approach the condition of equal population of states. Since the entropy is maximum in equilibrium, the discussion of the approach to equilibrium is equivalent to a discussion of the increase in entropy.

In quantum statistical mechanics there are two distinct causes for the increase in entropy. The first of these is a characteristic quantum mechanical effect with no analogue in classical mechanics. This cause of entropy increase, which may be designated as "fine-grain spreading", is due to the tendency of a single quantum mechanical system to spread over its various possible states. Thus, if a precisely defined system is localized in a given state by a precise measurement at $t = 0$ then another precise measurement at a later time has a certain probability of finding the system in any of a number of states. This spreading of the fine-grained density leads to an increase of the quantity $-k \sum_j W_j \ln W_j$ (cf. Klein), whereas the analogous classical quantity is constant in time by Liouville's theorem. It will be appreciated that this spreading of the fine-grained density is intimately connected with the perturbation caused in the system by the process of measurement. The second distinct cause of the increase in entropy is the complete analogue of the classical situation, and is

* The essential ideas underlying the method used in this Section appear in the books of von Mises and of Jeffreys and Jeffreys.

associated with the spreading of the coarse-grained density. This cause of entropy increase is a purely statistical property of the ensemble, and is, as in classical mechanics, quite independent of the measuring process.

In a given case either the "fine-grain spreading" or the "coarse-grain spreading" may be the dominant cause of the observed increase in entropy. If the system is an extremely complex one, such as a liter of a gas, we may expect statistical considerations to be important, and we may also expect the perturbation of the system by a measurement to be relatively small. For such complex systems we may therefore expect the coarse-grain spreading to be the dominant cause of entropy increase. Thus, Pauli and Fierz have shown that if the system is such that there are a very large number of states in each of the distinguishable groups discussed in Section 2, then the coarse-grain spreading alone is sufficient to account for the increase of the entropy to its equilibrium value (cf. Pauli and Fierz). If, on the other hand, the system is small and simple, such as a system composed of only a very few atoms, then the perturbation caused by a measurement of state is apt to be relatively large. We may thus expect the fine-grain spreading to be the dominant feature in this case. The systems dealt with in thermodynamics are almost always of the very large and complex type, so that the effect of the measurement itself on the increase of entropy is negligible. Were this not so then thermodynamics could not have been satisfactorily developed as a classical discipline even before the advent of quantum mechanics.

We shall now show that the form of the transition matrix is sufficient to insure the approach of a system to its equilibrium condition. We will find it convenient to assume that periodic measurements are made

on the system, though it will be appreciated from our remarks above that, for the systems usually treated in thermodynamics, these periodic measurements do not appreciably affect the approach to equilibrium. We also adopt the somewhat arbitrary convention that after each measurement a new ensemble is chosen to correspond to the information yielded by that measurement alone. This serves to re-diagonalize the density matrix at each measurement, to the great simplification of the analysis. We thus state our problem in the following way. We assume that at $t = 0$ an ensemble is set up to correspond to some arbitrary density vector. Periodic measurements, say at $t = 1, 2, \dots, n, \dots$ are then made on the system, supplying us with the sequence of coarse-grained density vectors

$$\vec{\rho}(0), \vec{\rho}(1), \vec{\rho}(2), \dots, \vec{\rho}(n), \dots \quad (7-1)$$

We inquire as to whether

$$\lim_{n \rightarrow \infty} \vec{\rho}(n) = \frac{1}{N} \vec{I} \quad (7-2)$$

By (2-9) we have

$$\vec{\rho}(1) = \{T(1)\} \cdot \vec{\rho}(0) \quad (7-3)$$

$$\vec{\rho}(2) = \{T(1)\} \cdot \vec{\rho}(1) = \{T(1)\}^2 \cdot \vec{\rho}(0) \quad (7-4)$$

so that the sequence (7-1) may be written

$$\vec{\rho}(0), \{T(1)\} \cdot \vec{\rho}(0), \{T(1)\}^2 \cdot \vec{\rho}(0), \dots, \{T(1)\}^n \cdot \vec{\rho}(0), \dots \quad (7-5)$$

and (7-2):

$$\lim_{n \rightarrow \infty} \{T(1)\}^n \cdot \vec{\rho}(0) = \frac{1}{N} \vec{I} \quad (7-6)$$

We consider now certain conceivable forms of the transition matrix $\{T(1)\}$. We distinguish three separate forms, which may be called intransitive, quasi-transitive, and transitive forms. We shall show that

It will be appreciated that the states are broken up into groups such that the passage of systems from certain groups to certain other groups is possible, but that the reverse passage is impossible. We might thus expect an accumulation of the systems of the ensemble into one or more such groups of states, eventually leaving all other groups of states unoccupied. We now show that no such form of the transition matrix is possible. For consider a block of elements such as that appearing in the upper left hand corner of the indicated matrix. Because of (2-10) we see that the sum of all the elements in any column of this block must be unity. But because there are additional non-zero elements in the first and second rows but not included in the block, and because these elements must be positive, the sum of the elements in any row of the block must be less than unity. That is, for such a block

$$\sum_j^M T_{jk} = 1 \quad (7-7)$$

and

$$\sum_k^M T_{jk} < 1 \quad (7-8)$$

where M is the number of rows, or columns, in the block. Summing (7-7) over k we obtain

$$\sum_k^M \sum_j^M T_{jk} = M \quad (7-9)$$

and summing (7-8) over j we obtain

$$\sum_j^M \sum_k^M T_{jk} < M \quad (7-10)$$

But (7-9) and (7-10) are inconsistent, so that we are forced to the

conclusion that a transition matrix cannot be in the quasi-transitive form.

By a transitive matrix we mean simply any matrix which is neither intransitive nor quasi-transitive. According to the reasoning above we are justified in taking every proper transition matrix as transitive.

We may now return to our evaluation of $\lim_{n \rightarrow \infty} \{T(1)\}^n \cdot \vec{p}(0)$.

Consider the set of eigenvectors $\vec{\omega}_\gamma$, $\gamma=1,2,\dots$ and the corresponding set of eigen-values λ_γ , $\gamma=1,2,\dots$ of the matrix $\{T(1)\}$. We have seen that the uniform distribution

$$\vec{\omega}_0 \equiv \frac{1}{N} \vec{I} \quad (7-11)$$

is an eigenvector of $\{T(1)\}$ with the eigenvalue $\lambda_0 = 1$. It is easily seen that this is the only eigenvector which corresponds to a physically realizable density vector. For, by the orthogonality of the eigenvectors we have

$$\vec{\omega}_\gamma \cdot \vec{\omega}_0 = 0 \quad \gamma \neq 0 \quad (7-12)$$

$$\text{or} \quad \sum_j \omega_{\gamma j} = 0 \quad \gamma \neq 0 \quad (7-13)$$

where $\omega_{\gamma j}$ indicates the j^{th} component of $\vec{\omega}_\gamma$. Thus it is impossible for all the components of $\vec{\omega}_\gamma$ to be real and non-negative, so that $\vec{\omega}_\gamma$ is not a physical density vector.

We may also show that $|\lambda_\gamma| < 1$ if $\gamma \neq 0$. For let $\omega_{\gamma k}$ be the component of $\vec{\omega}_\gamma$ with the largest absolute value. Because $\vec{\omega}_\gamma$ is an eigenvector we have

$$\lambda_\gamma \omega_{\gamma k} = \sum_j T_{jk}(1) \omega_{\gamma j} \quad (7-14)$$

$$\text{or} \quad \lambda_\gamma = \sum_j T_{jk}(1) \frac{\omega_{\gamma j}}{\omega_{\gamma k}} \quad (7-15)$$

$$\text{whence} \quad |\lambda_\gamma| \leq \sum_j T_{jk}(1) \frac{|\omega_{\gamma j}|}{|\omega_{\gamma k}|} \quad (7-16)$$

But we have assumed

$$\frac{|\omega_{\gamma j}|}{|\omega_{\gamma k}|} \leq 1 \quad (7-17)$$

and we have by (2-10)

$$\sum_j T_{jk}(1) = 1 \quad (7-18)$$

so that it follows that

$$|\lambda_\gamma| \leq 1 \quad (7-19)$$

Furthermore, the equality sign in (7-19) can hold only if $T_{jk}(1) = 0$

whenever $|\omega_{\gamma j}| \div |\omega_{\gamma k}| \leq 1$, a case which is excluded because $\{T\}$ is

transitive, or if $\gamma = 0$ so that $\omega_{\gamma j} = \omega_{\gamma k}$ for all j . We thus may rewrite

(7-19) more explicitly as

$$|\lambda_\gamma| < 1 \quad \gamma \neq 0 \quad (7-20)$$

Now, let the expansion of the initial density vector $\vec{\rho}(0)$ in terms of the eigenvectors $\vec{\omega}_\gamma$ be

$$\vec{\rho}(0) = \vec{\omega}_0 + \sum_{\gamma=1,2,\dots} c_\gamma \vec{\omega}_\gamma \quad (7-21)$$

The coefficient of $\vec{\omega}_0$ is easily seen to be unity, for we must have

$\vec{\rho}(0) \cdot \vec{I} = 1$ and we have by (7-11) and (7-12) that $\vec{\omega}_\gamma \cdot \vec{I} = \delta_{\gamma 0}$.

$$\text{Thus} \quad \{T(1)\}^n \cdot \vec{\rho}(0) = \vec{\omega}_0 + \sum_{\gamma=1,2,\dots} c_\gamma \lambda_\gamma^n \vec{\omega}_\gamma \quad (7-22)$$

and since, by (7-20)

$$\lim_{n \rightarrow \infty} \lambda_\gamma^n = 0 \quad \gamma \neq 0 \quad (7-23)$$

we have

$$\lim_{n \rightarrow \infty} \{T(1)\}^n \cdot \vec{\rho}(0) = \vec{\omega}_0 = \frac{1}{N} \vec{1} \quad (7-24)$$

We have thus shown that an ensemble initially set up in accordance with any arbitrary density vector will approach the condition of equal population of all states, that is, will approach the equilibrium condition.

With respect to the conditions under which it is possible to have an equality sign in (7-19), there exists, in addition to the case $\gamma = 0$ discussed above, another possibility. That is, we may have $|\omega_{\gamma j}| = |\omega_{\gamma k}|$ for all j even though $\omega_{\gamma j} \neq \omega_{\gamma k}$. It may be seen that such a case arises if the transition matrix is a cyclic matrix, the elements of which are all either unity or zero. If the transition matrix is of this form then a system which is known to be in a particular state at $t = 0$ will pass in turn through each of the states and will return to the original state at $t = N$. Such a system will not approach the equilibrium condition of equal population of states, and a cyclic matrix must thus be regarded as an exceptional case.

8 - The Principle of Dynamical Reversibility

The Principle of Dynamical Reversibility is a well-known theorem in both classical and quantum mechanics. Onsager has used this principle as the basis of his derivation of the Reciprocal Relations, and it therefore seems appropriate to briefly review the principle here.

As before, we shall be chiefly interested in the case in which the observable x is classically an even function of the momenta and of an externally applied magnetic field, and in this case the Principle of Dynamical Reversibility takes a particularly simple form. If x is an even function of the momenta and field then the principle states that for any system

$$\bar{x}(t,A) = \bar{x}(-t,-A) \quad (8-1)$$

where $\bar{x}(t,A)$ is the observed value of x at time t if the external magnetic vector potential has the value A .

It may be easily seen that this form of the principle follows immediately from our formalism. For if x is an even function of the momenta and magnetic field then we have by (3-27)

$$\{T(t,A)\}^\dagger = \{T(t,-A)\} \quad (8-2)$$

Also, by (2-12)

$$\{T(t,A)\}^\dagger = \{T(-t,A)\} \quad (8-3)$$

whence, combining (8-2) and (8-3)

$$\{T(t,A)\} = \{T(-t,-A)\} \quad (8-4)$$

Now, if \vec{x} denotes a "vector" whose components are the eigenvalues of \underline{x} in the states ϕ_1 , then the expectation value of x is

$$\bar{x}(t,A) = \vec{x} \cdot \vec{\rho}(t,A) \quad (8-5)$$

$$\text{or} \quad \bar{x}(t,A) = \vec{x} \cdot \{T(t,A)\} \cdot \vec{\rho}(0) \quad (8-6)$$

and by (8-4) we immediately obtain our result

$$\bar{x}(t,A) = \bar{x}(-t,-A) \quad (8-7)$$

9 - Onsager's Reciprocal Relations

Having considered at some length the general formalism of the time-dependence of ensembles, we now turn our attention specifically to the important Reciprocal Relations of Onsager. These relations are the expressions of a symmetry in the mutual interference of two irreversible processes occurring simultaneously in a system. In this section we shall briefly review the elegant derivation given by Onsager, and we shall obtain an alternative derivation in terms of our previous formalism. In succeeding sections we shall discuss the Reciprocal Relations and their application in detail.

a - Onsager's Derivation of the Reciprocal Relations

We shall partially quote the concise review of Onsager's derivation as given by Casimir:

Consider a number of variables x^i ($i=1,2,\dots,n$) which in equilibrium assume values x_o^i .

$$\text{Let } x^i = x_o^i + \alpha^i \quad (9-1)$$

The entropy in a state differing from the equilibrium state will be

$$S = S_o + \Delta S \quad (9-2)$$

where ΔS is of the form

$$\Delta S = -\frac{1}{2} \sum_{i,k} S_{ik} \alpha^i \alpha^k \quad (9-3)$$

where S_{ik} is a positive definite form. The probability distribution for the α^i is given by

$$W(\alpha^1, \dots, \alpha^n) d\alpha^1 \dots d\alpha^n = \frac{e^{\Delta S/k} d\alpha^1 \dots d\alpha^n}{\int \dots \int e^{\Delta S/k} d\alpha^1 \dots d\alpha^n} \quad (9-4)$$

Define

$$\gamma_i = \sum_k S_{ik} \alpha^k = - \frac{\delta \Delta S}{\delta \alpha^i} \quad (9-5)$$

then we may easily see that

$$\overline{\gamma_i \alpha^j} = k \delta_{ij} = \begin{cases} k & i = j \\ 0 & i \neq j \end{cases} \quad (9-6)$$

For if we denote by A the integral in the denominator of (9-4), then

$$\begin{aligned} \overline{\gamma_i \alpha^j} &= \frac{1}{A} \int \dots \int \gamma_i \alpha^j e^{\Delta S/k} d\alpha^1 \dots d\alpha^n \\ &= - \frac{1}{A} \int \dots \int \alpha^j \frac{\delta \Delta S}{\delta \alpha^i} e^{\Delta S/k} d\alpha^1 \dots d\alpha^n \\ &= - \frac{k}{A} \int \dots \int \alpha^j \frac{\delta}{\delta \alpha^i} e^{\Delta S/k} d\alpha^1 \dots d\alpha^n \end{aligned}$$

and integrating by parts, with respect to α^i

$$\overline{\gamma_i \alpha^j} = - \frac{k}{A} \int \dots \int \frac{\delta}{\delta \alpha^i} [\alpha^j e^{\Delta S/k}] d\alpha^1 \dots d\alpha^n + \frac{k}{A} \int \dots \int e^{\Delta S/k} \frac{\delta \alpha^j}{\delta \alpha^i} d\alpha^1 \dots d\alpha^n$$

and since both $e^{\Delta S/k}$ and $\alpha^i e^{\Delta S/k}$ must vanish at $\alpha^i = \pm \infty$ the first integral vanishes. The second integral is obviously equal to $k\delta_{ij}$, so that we obtain (9-6).

Suppose now that there is no external magnetic field, and that the α^i are even functions of the momenta of the particles composing the system, then, by the Principle of Dynamical Reversibility, the future behavior of a system having specified values of α^i at a time t , on the

average, is identical with its past behavior:

$$\overline{\alpha^k(t + \tau)}_{\alpha^1(t) \dots \alpha^n(t)} = \overline{\alpha^k(t - \tau)}_{\alpha^1(t) \dots \alpha^n(t)} \quad (9-7)$$

the suffixes denoting that the values remain fixed, so that the average is taken over a section of the microcanonical ensemble corresponding to these values. Multiplying by $\alpha^j(t)$ and taking the average over all possible values of $\alpha^1(t) \dots \alpha^n(t)$ we find

$$\overline{\alpha^j(t) \alpha^k(t + \tau)} = \overline{\alpha^j(t) \alpha^k(t - \tau)} \quad (9-8)$$

Consider now the macroscopic equations governing an irreversible process (e.g., Ohm's Law, Fick's Law, etc.). These are of the form

$$\dot{\alpha}^i = \sum_k L_k^i \alpha_k \quad (9-9)$$

and may be transformed by (9-5) into the form

$$\dot{\alpha}^i = \sum_k p^{ik} \gamma_k \quad (9-10)$$

Assume that these same equations also describe the average behavior of fluctuations in the following sense: there exists a time interval τ_1 such that for $\tau > \tau_1$, but $\tau \ll T$ (where T is the time in which, according to our equations, a disturbance of equilibrium is appreciably reduced),

$$\overline{\alpha^i(t + \tau)}_{\alpha^1(t) \dots \alpha^n(t)} - \alpha^i(t) = \tau \sum_k p^{ik} \gamma_k(t) \quad (9-11)$$

Now, having (9-6), (9-8), and (9-11) we are equipped to obtain our result. Multiplying (9-11) by $\alpha^j(t)$ and taking the average we find

$$\overline{\alpha^j(t) \alpha^i(t + \tau)} - \alpha^i(t) = \tau \cdot p^{ij} \cdot k \quad (9-12)$$

and similarly

$$\overline{\alpha^i(t) [\alpha^j(t+\tau) - \alpha^j(t)]} = \tau p^{ji} \cdot k \quad (9-13)$$

But according to (9-8) the left-hand sides of these equations are equal; hence

$$p^{ji} = p^{ij} \quad (9-14)$$

This is Onsager's fundamental relation. If a magnetic field is present (9-14) must be replaced by

$$p^{ji}(A) = p^{ij}(-A) \quad (9-15)$$

We may now give the Onsager Relations a more precise statement than we were able to before. The substance of the Reciprocal Relations, in the absence of a magnetic field, is that the macroscopic equations (9-10) are symmetric provided the independent variables γ_k are chosen as the variables conjugate to the α^k in the sense of (9-5).

b - Alternative Derivation of the Onsager Relations

Although Onsager's derivation of the Reciprocal Relations is very elegant it is felt that additional insight can be obtained through an alternative derivation based on the formalism of the preceding sections. Furthermore, since some question has been raised as to the validity of Onsager's use of fluctuations in an ensemble for an analysis of macroscopic irreversible processes (cf. Casimir), it seems desirable to have a derivation which does not involve this recourse to fluctuations. The derivation to be given bears a similarity to the analysis of the chemical monomolecular triangle reaction cited by Onsager as an analogy to the Reciprocal Relations (cf. Onsager p. 410).

We consider, for simplicity, two variables $x^{(1)}$ and $x^{(2)}$ both of which are to be even functions of the momenta of the particles composing the system and of the magnetic field.

It is evident that the functions ϕ_i of Section 1 could be chosen as the simultaneous eigenfunctions of $\underline{x}^{(1)}$ and $\underline{x}^{(2)}$, so that the generalization from a single variable to several variables $x^{(i)}$ has no significant effect on the analysis of the preceding sections (for the resolution of the difficulties which might arise if $\underline{x}^{(1)}$ and $\underline{x}^{(2)}$ did not commute, see von Neumann, who shows that such "macroscopic operators" can be defined so as to be commutable).

We now suppose that some external restraint is imposed on the system requiring the expectation value of $x^{(1)}$ to be $\overline{x^{(1)}}$ and the expectation value of $x^{(2)}$ to be $\overline{x^{(2)}}$. If $x^{(1)}$ were to denote the volume this restraint might simply be a piston applying a pressure; or if $x^{(1)}$ were to denote the energy of the system the restraint might arise by the system being in contact with a heat reservoir. Such restraints play a familiar and fundamental role in the theory of statistical mechanics. We assume that the system is in equilibrium with respect to these restraints. Then, as in the usual equilibrium theory, the coarse-grained density vector $\vec{\rho}$ may be obtained by maximizing

$$S = -k \sum_j \rho_j \ln \rho_j \quad (9-16)$$

subject to the auxiliary conditions

$$\begin{aligned} \overline{x^{(1)}} &= \sum_j x_j^{(1)} \rho_j = \vec{x}^{(1)} \cdot \vec{\rho} \\ \overline{x^{(2)}} &= \sum_j x_j^{(2)} \rho_j = \vec{x}^{(2)} \cdot \vec{\rho} \\ 1 &= \sum_j \rho_j = \vec{I} \cdot \vec{\rho} \end{aligned} \quad (9-17)$$

Thus we find that in the condition of "restrained equilibrium"

$$\rho_j = e^{-\frac{\lambda}{k} - \frac{\gamma^{(1)}}{k} x_j^{(1)} - \frac{\gamma^{(2)}}{k} x_j^{(2)}} \quad (9-18)$$

where the $\frac{\lambda}{k}$, $\frac{\gamma^{(1)}}{k}$, and $\frac{\gamma^{(2)}}{k}$ are Lagrange Multipliers and are functions of $\overline{x^{(1)}}$ and $\overline{x^{(2)}}$, and where Boltzmann's constant k is introduced here for the sake of future convenience.

The entropy in the restrained equilibrium condition is, by (9-18) and (9-16)

$$S = \lambda + \gamma^{(1)} \overline{x^{(1)}} + \gamma^{(2)} \overline{x^{(2)}} \quad (9-19)$$

We now assume that at time $t = 0$ the restraint is lifted, and the expectation values of $x^{(1)}$ and $x^{(2)}$ begin to change in the directions of their values at absolute equilibrium. It is the manner in which these expectation values change that we wish to study. We have, as in (8-6):

$$\begin{aligned} \overline{x^{(1)}}(t) - \overline{x^{(1)}}(0) &= \overline{x^{(1)}} \cdot \{T(t)\} \cdot \overline{\beta}(0) - \overline{x^{(1)}} \cdot \overline{\beta}(0) \\ &= \sum_j \sum_k x_j^{(1)} T_{jk}(t) \rho_k(0) - \sum_j x_j^{(1)} \rho_j(0) \end{aligned}$$

and because $\sum_k T_{jk} = 1$ we can write this as

$$\begin{aligned} \overline{x^{(1)}}(t) - \overline{x^{(1)}}(0) &= \sum_j \sum_k x_j^{(1)} [\rho_k(0) - \rho_j(0)] T_{jk}(t) \\ \text{and} \quad \overline{x^{(2)}}(t) - \overline{x^{(2)}}(0) &= \sum_j \sum_k x_j^{(2)} [\rho_k(0) - \rho_j(0)] T_{jk}(t) \end{aligned} \quad (9-20)$$

At $t = 0$ the system is in the condition of restrained equilibrium, so that $\rho_j(0)$ is given by (9-18). We now make the assumption that the condition of restrained equilibrium is not a large deviation from the condition of absolute equilibrium. Since in absolute equilibrium, by (6-1),

$$\rho_j = \frac{1}{N} \quad (9-21)$$

where N is the number of states of the system, then if we write (9-20) in the form

$$\rho_j(0) = \frac{1}{N} e^{\ln N - \frac{\lambda}{k} - \frac{\gamma^{(1)}}{k} x_j^{(1)} - \frac{\gamma^{(2)}}{k} x_j^{(2)}} \quad (9-22)$$

we assume that the exponential is very nearly unity. Expanding this exponential in a series, we obtain, approximately

$$\rho_j(0) = \frac{1}{N} \left[1 + \ln N - \frac{\lambda}{k} - \frac{\gamma^{(1)}}{k} x_j^{(1)} - \frac{\gamma^{(2)}}{k} x_j^{(2)} \right]$$

Thus equations (9-20) take the simple form:

$$\begin{aligned} \overline{x^{(1)}(t)} - \overline{x^{(1)}(0)} &= \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} \left[-\gamma^{(1)} x_k^{(1)} - \gamma^{(2)} x_k^{(2)} + \right. \\ &\quad \left. + \gamma^{(1)} x_j^{(1)} + \gamma^{(2)} x_j^{(2)} \right] T_{jk}(t) \end{aligned} \quad (9-23)$$

$$\begin{aligned} \overline{x^{(2)}(t)} - \overline{x^{(2)}(0)} &= \sum_j \sum_k x_j^{(2)} \frac{1}{Nk} \left[-\gamma^{(1)} x_k^{(1)} - \gamma^{(2)} x_k^{(2)} + \right. \\ &\quad \left. + \gamma^{(1)} x_j^{(1)} + \gamma^{(2)} x_j^{(2)} \right] T_{jk}(t) \end{aligned}$$

or

$$\frac{\delta \overline{x^{(1)}}}{\delta t} = \frac{\overline{x^{(1)}(t)} - \overline{x^{(1)}(0)}}{t} = L_{11} \gamma^{(1)} + L_{12} \gamma^{(2)} \quad (9-24)$$

$$\frac{\delta \overline{x^{(2)}}}{\delta t} = \frac{\overline{x^{(2)}(t)} - \overline{x^{(2)}(0)}}{t} = L_{21} \gamma^{(1)} + L_{22} \gamma^{(2)}$$

where

$$\begin{aligned}
 L_{11}(A) &= \frac{1}{t} \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} (x_j^{(1)} - x_k^{(1)}) T_{jk}(t, A) \\
 L_{12}(A) &= \frac{1}{t} \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} (x_j^{(2)} - x_k^{(2)}) T_{jk}(t, A) \\
 L_{21}(A) &= \frac{1}{t} \sum_j \sum_k x_j^{(2)} \frac{1}{Nk} (x_j^{(1)} - x_k^{(1)}) T_{jk}(t, A) \\
 L_{22}(A) &= \frac{1}{t} \sum_j \sum_k x_j^{(2)} \frac{1}{Nk} (x_j^{(2)} - x_k^{(2)}) T_{jk}(t, A)
 \end{aligned} \tag{9-25}$$

Before considering the symmetry of L_{12} and L_{21} we want to establish the parallel with Onsager's analysis by showing that the variables $\gamma^{(1)}$ and $\gamma^{(2)}$ may be obtained from the entropy function just as in (9-5). We have

$$S = -k \sum_j \rho_j \ln \rho_j$$

whence, recalling that $\sum_j \delta \rho_j = 0$,

$$\delta S = -k \sum_j \ln \rho_j \delta \rho_j \tag{9-26}$$

$$= \sum_j [\lambda + \gamma^{(1)} x_j^{(1)} + \gamma^{(2)} x_j^{(2)}] \delta \rho_j$$

$$= \gamma^{(1)} \delta \bar{x}^{(1)} + \gamma^{(2)} \delta \bar{x}^{(2)} \tag{9-27}$$

so that

$$\gamma^{(1)} = \frac{\delta S}{\delta \bar{x}^{(1)}}$$

(9-28)

$$\gamma^{(2)} = \frac{\delta S}{\delta \bar{x}^{(2)}}$$

and $\gamma^{(1)}$ and $\gamma^{(2)}$ therefore correspond to Onsager's conjugate variables (9-5).

We may now consider the symmetry of L_{12} and L_{21} . Consider

$L_{12}(A)$:

$$\begin{aligned} L_{12}(A) &= \frac{1}{t} \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} (x_j^{(2)} - x_k^{(2)}) T_{jk}(t, A) \\ &= \frac{1}{t} \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} x_j^{(2)} T_{jk}(t, A) - \frac{1}{t} \sum_j \sum_k \frac{1}{Nk} x_k^{(2)} T_{jk}(t, A) \end{aligned}$$

The first summation may equally well be written as $\frac{1}{t} \sum_j \sum_k x_j^{(1)} \frac{1}{Nk} x_j^{(2)} T_{jk}(t, -A)$

because $\sum_k T_{jk}(A) = \sum_k T_{jk}(-A) = 1$. In the second summation we

may interchange the roles of the dummy indices j and k , and recall that,

$$\text{by (3-6), } T_{jk}(t, A) = T_{kj}(t, -A) \quad (9-29)$$

so that we obtain

$$L_{12}(A) = \frac{1}{t} \sum_j \sum_k x_j^{(2)} \frac{1}{Nk} (x_j^{(1)} - x_k^{(1)}) T_{jk}(t, -A)$$

$$\text{or, } L_{12}(A) = L_{21}(-A) \quad (9-30)$$

In the special case in which the magnetic field vanishes

$$L_{12} = L_{21} \quad (9-31)$$

Recapitulating, we may say that, in the absence of a magnetic field, the macroscopic equations governing the decay of variables from their values in a condition of "restrained equilibrium" are symmetric if the independent variables are chosen according to (9-28), and if the condition of restrained equilibrium is a small deviation from absolute equilibrium. It is seen that the symmetry is a result of the symmetry of the transition matrix.

In a magnetic field the significance of the relation (9-30) may be expressed more explicitly in the following way; We may define symmetric and anti-symmetric combinations of the L's by

$$L_{12}^{(s)} = \frac{1}{2} [L_{12} + L_{21}] = L_{21}^{(s)} \quad (9-32)$$

$$L_{12}^{(a)} = \frac{1}{2} [L_{12} - L_{21}] = -L_{21}^{(a)}$$

and (9-30) gives

$$L_{12}^{(s)}(A) = L_{12}^{(s)}(-A) \quad (9-33)$$

$$L_{12}^{(a)}(A) = -L_{12}^{(a)}(-A)$$

so that the kinetic coefficients (i.e., the L's) can be decomposed into parts which have the same symmetry character with respect to both the field and the indices.

In concluding this section we point out the following slight extension of the Reciprocal Relations. If at $t = 0$ the restraints are not completely lifted, as we have assumed above, but are merely altered - say, from initial restraints of $\overline{x_{init}^{(1)}}$, $\overline{x_{init}^{(2)}}$ to the values $\overline{x_{final}^{(1)}}$, $\overline{x_{final}^{(2)}}$ - then the Reciprocal Relations are still valid providing we take as independent variables $(\gamma_{initial}^{(1)} - \gamma_{final}^{(1)})$ and $(\gamma_{initial}^{(2)} - \gamma_{final}^{(2)})$.

This is easily obtained by a rather trivial alteration of the proof given above.

10 - The Production of Entropy and The Dissipation Function

The irreversible processes to which the Onsager Relations apply differ from the "quasi-static" processes considered in thermodynamics in that these irreversible processes are accompanied by a production of entropy. The rate of production of the entropy may be expressed in terms of the "currents", $\frac{\bar{\delta x}^{(1)}}{\delta t}$ and $\frac{\bar{\delta x}^{(2)}}{\delta t}$, this expression being called the dissipation function (after an analogous function introduced by Lord Rayleigh in his study of the effects of frictional forces in mechanics: cf. Rayleigh; Onsager I, p. 421). In this section we shall examine certain characteristics of the dissipation function in the presence and in the absence of a magnetic field.

a - The Dissipation Function

The expression for the dissipation function may be easily obtained, for by (9-27)

$$\delta S = \gamma^{(1)} \bar{\delta x}^{(1)} + \gamma^{(2)} \bar{\delta x}^{(2)} \quad (10-1)$$

or

$$\frac{\delta S}{\delta t} = \gamma^{(1)} \frac{\bar{\delta x}^{(1)}}{\delta t} + \gamma^{(2)} \frac{\bar{\delta x}^{(2)}}{\delta t} \quad (10-2)$$

and in order to obtain $\frac{\delta S}{\delta t}$ as a function of the "currents" $\frac{\bar{\delta x}^{(i)}}{\delta t}$ we need only eliminate the "forces" $\gamma^{(i)}$ by the kinetic equations (9-24).

Solving the kinetic equations for the "forces":

$$\begin{aligned} \gamma^{(1)} &= R_{11} \frac{\bar{\delta x}^{(1)}}{\delta t} + R_{12} \frac{\bar{\delta x}^{(2)}}{\delta t} \\ \gamma^{(2)} &= R_{21} \frac{\bar{\delta x}^{(1)}}{\delta t} + R_{22} \frac{\bar{\delta x}^{(2)}}{\delta t} \end{aligned} \quad (10-3)$$

where

$$R_{11} = \frac{L_{22}}{L_{11}L_{22} - L_{12}L_{21}} \quad R_{12} = \frac{-L_{12}}{L_{11}L_{22} - L_{12}L_{21}} \quad (10-4)$$

$$R_{22} = \frac{L_{11}}{L_{11}L_{22} - L_{12}L_{21}} \quad R_{21} = \frac{-L_{21}}{L_{11}L_{22} - L_{12}L_{21}}$$

Substituting these values for the forces in our expression (10-2) for $\frac{\delta S}{\delta t}$ we obtain

$$\begin{aligned} \frac{\delta S}{\delta t} = & R_{11} \left(\frac{\delta \bar{x}^{(1)}}{\delta t} \right)^2 + (R_{12} + R_{21}) \cdot \frac{\delta \bar{x}^{(1)}}{\delta t} \cdot \frac{\delta \bar{x}^{(2)}}{\delta t} + \\ & + R_{22} \left(\frac{\delta \bar{x}^{(2)}}{\delta t} \right)^2 \end{aligned} \quad (10-5)$$

which is the dissipation function.

Alternatively, the rate of production of entropy may be expressed as a function of the forces:

$$\frac{\delta S}{\delta t} = L_{11} \gamma^{(1)2} + (L_{12} + L_{21}) \gamma^{(1)} \gamma^{(2)} + L_{22} \gamma^{(2)2} \quad (10-6)$$

b - Dissipation Function in Absence of Magnetic Field

In the absence of a magnetic field we have, by (9-31)

$$L_{12} = L_{21} \quad (10-7)$$

whence $R_{12} = R_{21}$ (10-8)

and the dissipation function becomes

$$\frac{\delta S}{\delta t} = R_{11} \left(\frac{\delta \bar{x}^{(1)}}{\delta t} \right)^2 + 2R_{12} \cdot \frac{\delta \bar{x}^{(1)}}{\delta t} \cdot \frac{\delta \bar{x}^{(2)}}{\delta t} + R_{22} \left(\frac{\delta \bar{x}^{(2)}}{\delta t} \right)^2 \quad (10-9)$$

The dissipation function may now be considered as playing the role of a "potential" similar to the potentials of thermodynamics. For we note that the "forces" may be obtained by differentiating the dissipation function with respect to the "currents". Thus

$$\frac{d \left(\frac{\delta S}{\delta t} \right)}{d \left(\frac{\delta x^{(1)}}{\delta t} \right)} = 2R_{11} \frac{\delta x^{(1)}}{\delta t} + 2R_{12} \frac{\delta x^{(2)}}{\delta t} = 2\gamma^{(1)} \quad (10-10)$$

and similarly for $\gamma^{(2)}$.

The statement that there exists an entropy dissipation function quadratic in the "currents", and that the "force" is the derivative of the dissipation function with respect to the "current", is equivalent to the statement of Onsager's Relations in the absence of a magnetic field. Onsager utilizes this fact to express the Reciprocal Relations in terms of a variation principle (cf. Onsager I, p. 420).

We may note here that the kinetic coefficients L_{ij} are not completely independent. It is a consequence of thermodynamics that we must have

$$L_{11}L_{22} - L_{12}^2 \geq 0 \quad (10-11)$$

This is the condition that

$$\frac{\delta S}{\delta t} = L_{11}\gamma^{(1)2} + 2L_{12}\gamma^{(1)}\gamma^{(2)} + L_{22}\gamma^{(2)2} \quad (10-12)$$

should be positive definite. If (10-11) were not true then it would be possible to have a spontaneously occurring process in which the entropy decreased, which is unthinkable. It is interesting to see, therefore, that our explicit formulae (9-25) for the kinetic coefficients do indeed

imply the condition $L_{11}L_{22} - L_{12}^2 \geq 0$. The formulae for the kinetic coefficients are

$$\begin{aligned} L_{11} &= \frac{1}{tN} \sum_j \sum_k x_j^{(1)} (x_j^{(1)} - x_k^{(1)}) T_{jk} \\ L_{12} &= \frac{1}{tN} \sum_j \sum_k x_j^{(1)} (x_j^{(2)} - x_k^{(2)}) T_{jk} \\ L_{22} &= \frac{1}{tN} \sum_j \sum_k x_j^{(2)} (x_j^{(2)} - x_k^{(2)}) T_{jk} \end{aligned} \quad (10-13)$$

Interchanging the dummy indices j and k and recalling that $T_{jk} = T_{kj}$

we obtain the alternative forms

$$\begin{aligned} L_{11} &= \frac{1}{tN} \sum_j \sum_k -x_k^{(1)} (x_j^{(1)} - x_k^{(1)}) T_{jk} \\ L_{12} &= \frac{1}{tN} \sum_j \sum_k -x_k^{(1)} (x_j^{(2)} - x_k^{(2)}) T_{jk} \\ L_{22} &= \frac{1}{tN} \sum_j \sum_k -x_k^{(2)} (x_j^{(2)} - x_k^{(2)}) T_{jk} \end{aligned} \quad (10-14)$$

Adding these two alternative expressions for the L_{ij} , and dividing by 2,

we obtain

$$\begin{aligned} L_{11} &= \frac{1}{2tN} \sum_j \sum_k (x_j^{(1)} - x_k^{(1)})^2 T_{jk} \\ L_{12} &= \frac{1}{2tN} \sum_j \sum_k (x_j^{(1)} - x_k^{(1)}) (x_j^{(2)} - x_k^{(2)}) T_{jk} \\ L_{22} &= \frac{1}{2tN} \sum_j \sum_k (x_j^{(2)} - x_k^{(2)})^2 T_{jk} \end{aligned} \quad (10-15)$$

Now, let

$$\begin{aligned} (x_j^{(1)} - x_k^{(1)}) \sqrt{\frac{T_{jk}}{2tN}} &= \lambda_{jk} \\ (x_j^{(2)} - x_k^{(2)}) \sqrt{\frac{T_{jk}}{2tN}} &= \mu_{jk} \end{aligned} \quad (10-16)$$

Then

$$\begin{aligned} L_{11} &= \sum_{jk} \lambda_{jk}^2 \\ L_{12} &= \sum_{jk} \lambda_{jk} \mu_{jk} \\ L_{22} &= \sum_{jk} \mu_{jk}^2 \end{aligned} \quad (10-17)$$

But the Schwartz Inequality states that

$$\left(\sum_{jk} \lambda_{jk}^2 \right) \left(\sum_{jk} \mu_{jk}^2 \right) \geq \left(\sum_{jk} \lambda_{jk} \mu_{jk} \right)^2 \quad (10-18)$$

or

$$L_{11} L_{22} \geq L_{12}^2 \quad (10-19)$$

which assures us that in any irreversible process the entropy cannot decrease.

c - Dissipation Function in a Magnetic Field

In the presence of a magnetic field it is no longer possible to obtain the forces by differentiation of the dissipation function with respect to the currents. It is, however, possible to consider the current as the sum of a dissipative part and a non-dissipative part, and the forces can then be obtained by differentiation of the dissipation function with respect to the dissipative currents. We shall see that the dissipative current, which contributes to the production of entropy,

is an even function of the magnetic field, whereas the non-dissipative current, which does not contribute to the production of entropy, is an odd function of the magnetic field. We shall also see that, subject to the assumption of initially random phases, it is impossible for a non-dissipative current to "flow" unaccompanied by a dissipative current.

The resolution of the currents into dissipative and non-dissipative parts is accomplished as follows: According to (9-32) the kinetic equations can be written in the form

$$\begin{cases} \frac{\delta \bar{x}^{(1)}}{\delta t} = L_{11} \gamma^{(1)} + [L_{12}^{(s)} + L_{12}^{(a)}] \gamma^{(2)} \\ \frac{\delta \bar{x}^{(2)}}{\delta t} = [L_{21}^{(s)} + L_{21}^{(a)}] \gamma^{(1)} + L_{22} \gamma^{(2)} \end{cases} \quad (10-20)$$

where

$$\begin{cases} L_{12}^{(s)} = L_{21}^{(s)} \\ L_{12}^{(a)} = -L_{21}^{(a)} \end{cases} \quad (10-21)$$

and

$$\begin{cases} L_{12}^{(s)}(A) = L_{12}^{(s)}(-A) \\ L_{12}^{(a)}(A) = -L_{12}^{(a)}(-A) \end{cases} \quad (10-22)$$

Substituting (10-20) into our formula for the rate of production of entropy:

$$\begin{aligned} \frac{\delta S}{\delta t} &= \gamma^{(1)} \frac{\delta \bar{x}^{(1)}}{\delta t} + \gamma^{(2)} \frac{\delta \bar{x}^{(2)}}{\delta t} \\ &= \gamma^{(1)} [L_{11} \gamma^{(1)} + L_{12}^{(s)} \gamma^{(2)} + L_{12}^{(a)} \gamma^{(2)}] + \\ &\quad + \gamma^{(2)} [L_{21}^{(s)} \gamma^{(1)} + L_{21}^{(a)} \gamma^{(1)} + L_{22} \gamma^{(2)}] \end{aligned}$$

and, by the symmetry property (10-21),

$$\begin{aligned} \frac{\delta S}{\delta t} = & \gamma^{(1)} L_{11} \gamma^{(1)} + L_{12}^{(s)} \gamma^{(2)} + \\ & + \gamma^{(2)} L_{21}^{(s)} \gamma^{(1)} + L_{22} \gamma^{(2)} \end{aligned} \quad (10-23)$$

We thus see that the resolution of the currents into dissipative and non-dissipative parts may be made as follows:

$$\frac{\delta \bar{x}^{(i)}}{\delta t} = J_d^{(i)} + J_n^{(i)} \quad (10-24)$$

and

$$J_d^{(1)} \equiv L_{11} \gamma^{(1)} + L_{12}^{(s)} \gamma^{(2)} \quad (10-25)$$

$$J_d^{(2)} \equiv L_{21}^{(s)} \gamma^{(1)} + L_{22} \gamma^{(2)}$$

$$J_n^{(1)} \equiv L_{12}^{(a)} \gamma^{(2)} \quad (10-26)$$

$$J_n^{(2)} \equiv L_{21}^{(a)} \gamma^{(1)}$$

The dependence of the partial currents on the magnetic field follows at once from (10-22). For fixed values of the forces we see that

$$\begin{aligned} J_d^{(1)}(A) &= J_d^{(1)}(-A) \\ J_n^{(1)}(A) &= -J_n^{(1)}(-A) \end{aligned} \quad (10-27)$$

so that the dissipative currents are even functions of the field, and the non-dissipative currents are odd functions of the field. Accordingly, for small values of the field, the non-dissipative currents will be proportional to the magnetic vector potential.

The dissipation function may now be written as

$$\frac{\delta S}{\delta t} = \gamma^{(1)} J_d^{(1)} + \gamma^{(2)} J_d^{(2)} \quad (10-28)$$

We may also express the dissipation function as a quadratic function of the dissipative currents by eliminating the forces by equations (10-25). Solving these equations for the forces:

$$\gamma^{(1)} = R_{11}^{(s)} J_d^{(1)} + R_{12}^{(s)} J_d^{(2)} \quad (10-29)$$

$$\gamma^{(2)} = R_{21}^{(s)} J_d^{(1)} + R_{22}^{(s)} J_d^{(2)}$$

where

$$R_{11}^{(s)} = \frac{L_{22}}{L_{11}L_{22} - L_{12}^{(s)}L_{21}^{(s)}} \quad R_{12}^{(s)} = \frac{-L_{12}^{(s)}}{L_{11}L_{22} - L_{12}^{(s)}L_{21}^{(s)}} \quad (10-30)$$

$$R_{22}^{(s)} = \frac{L_{11}}{L_{11}L_{22} - L_{12}^{(s)}L_{21}^{(s)}} \quad R_{21}^{(s)} = \frac{-L_{21}^{(s)}}{L_{11}L_{22} - L_{12}^{(s)}L_{21}^{(s)}}$$

and

$$R_{12}^{(s)} = R_{21}^{(s)} \quad (10-31)$$

Substituting these values for the forces in our expression (10-28) for $\frac{\delta S}{\delta t}$ we obtain the dissipation function:

$$\frac{\delta S}{\delta t} = R_{11}^{(s)} J_d^{(1)2} + 2R_{12}^{(s)} J_d^{(1)} J_d^{(2)} + R_{22}^{(s)} J_d^{(2)2} \quad (10-32)$$

It is now evident that, in analogy to the situation in the absence of a magnetic field, the forces can be obtained by differentiation of the dissipation function with respect to the dissipative currents.

For

$$\frac{d\left(\frac{\delta S}{\delta t}\right)}{d J_d^{(1)}} = 2R_{11}^{(s)} J_d^{(1)} + 2R_{12}^{(s)} J_d^{(2)} = 2\gamma^{(1)} \quad (10-33)$$

and similarly for $\gamma^{(2)}$.

In conclusion of this Section, we note that it is impossible for a non-dissipative current to "flow" unaccompanied by a dissipative current. Physically this is evident, for if a non-dissipative current were to flow alone then a deviation from equilibrium would vanish without the production of entropy. However, it is well to inquire as to how this restriction arises formally, and this can be seen as follows:

Just as we have formed symmetric and anti-symmetric combinations of the kinetic coefficients, we may form symmetric and anti-symmetric combinations of the transition elements T_{jk} . Thus

$$\begin{aligned} T_{jk}^{(s)} &= \frac{1}{2} [T_{jk} + T_{kj}] = T_{kj}^{(s)} \\ T_{jk}^{(a)} &= \frac{1}{2} [T_{jk} - T_{kj}] = -T_{kj}^{(a)} \end{aligned} \quad (10-34)$$

Then the T_{jk} appearing in our equations (9-25) for the kinetic coefficients can be eliminated in favor of the symmetric and anti-symmetric combinations $T_{jk}^{(s)}$ and $T_{jk}^{(a)}$. In this way one may obtain

$$L_{11} = \frac{1}{2tN} \sum_j \sum_k (x_j^{(1)} - x_k^{(1)})^2 T_{jk}^{(s)} \quad (10-35)$$

and

$$L_{12}^{(a)} = \frac{1}{tN} \sum_j \sum_k x_j^{(1)} (x_j^{(2)} - x_k^{(2)}) T_{jk}^{(a)}$$

so that the kinetic coefficients contributing to the dissipative current involve the symmetric combination $T_{jk}^{(s)}$, whereas the kinetic coefficients contributing to the non-dissipative current involve the anti-symmetric combination $T_{jk}^{(a)}$. However, the condition

$$T_{jk} \geq 0$$

requires that if $T_{jk}^{(s)} = 0$ then also $T_{jk}^{(a)} = 0$, as can be easily seen from (10-34). Now, if the dissipative current vanishes then L_{11} must vanish, and we see by (10-35) that every $T_{jk}^{(s)}$ must vanish. This requires that every $T_{jk}^{(a)}$ also vanish, and thus in turn $L_{12}^{(a)}$, and finally the non-dissipative current, must also vanish. We thus verify that the vanishing of the dissipative current requires the vanishing of the non-dissipative current. It should, however, be noted that this conclusion is a result of the non-negative character of the transition elements which is, in turn, connected with the assumption of initial diagonality of the density matrix. Thus, if the specification of the initial condition of the system were such as to not correspond to random phases, our present argument would no longer lead to the conclusion stated.

11 - Steady State Response

Among the most interesting of irreversible processes, from a theoretical standpoint, are those which occur in a steady state. Applications of Reciprocal Relations to such processes have been made by Onsager and by Casimir. In addition, many authors have studied such processes by a quasi-thermodynamic method due to Kelvin, and equivalent results are obtained by both of these methods. We shall see in this Section that the application of Onsager's Relations to steady-state processes involves a fundamental approximation, which we shall examine in some detail. Consideration of the quasi-thermodynamic method shows that it is based on precisely this same approximation.

That the Onsager Relations do not apply rigorously to steady-state processes may be seen in terms of either of the derivations given in Section 9. Thus, in the derivation based on the transition matrix it is explicitly postulated that the irreversible process is one which follows the removal of some restraint with which the system is originally in equilibrium. This postulate appears explicitly in the derivation in the assumption that the initial value of the density vector ρ is given by the value which the density vector would have if the system were in equilibrium with the restraints, i.e.,

$$\rho_j = e^{-\lambda - \frac{\gamma^{(1)}}{k} x_j^{(1)} - \frac{\gamma^{(2)}}{k} x_j^{(2)}} .$$

Now, a steady-state process

depends upon the existence of some mechanism such that as the irreversible process tends to change $\vec{\rho}$ from its restrained equilibrium value $e^{(-\lambda \dots)}$, this mechanism tends always to bring $\vec{\rho}$ back to the restrained equilibrium value. The competition between the

irreversible process and the restoring mechanism results in the maintenance of $\vec{\rho}$ at some steady-state value. If this steady-state value were the restrained equilibrium value $e^{(-\lambda-\dots)}$ then the application of Onsager's Relations would be quite rigorous. However, it is clear that the competition between irreversible process and restoring mechanism will result in the steady-state value of $\vec{\rho}$ deviating somewhat from the restrained equilibrium value. Obviously the goodness of the approximation made in the application of Onsager's Relations depends upon the smallness of this deviation of the steady-state value of $\vec{\rho}$ from the restrained equilibrium value. We shall make a detailed analysis of the application of Onsager's Relations to a specific irreversible process in order to clarify the specific nature of the approximation made.

Before undertaking this analysis we may note that in terms of Onsager's derivation of the Reciprocal Relations the situation is essentially the same as described above, although the restrictions are not quite so evident. In Onsager's derivation it is assumed that

$$(see 9-11) \quad \overline{\alpha^1(t+\tau)}_{\alpha^1(t)\dots\alpha^n(t)} - \alpha^1(t) = \tau \sum_k p^{1k} \gamma_k(t)$$

where the averaging process is to be carried out over the portion of the ensemble corresponding to the values $\alpha^1(t), \alpha^2(t), \dots, \alpha^n(t)$. Now the only system which may be expected to exhibit properties corresponding to the average over this portion of the ensemble is a system which is in equilibrium with respect to the restraints $\alpha^1(t), \alpha^2(t), \dots, \alpha^n(t)$. Thus in this derivation the restriction to the condition of restrained equilibrium appears implicitly in the form of the averaging process.

We may now consider in some detail the application of Onsager's Relations to a specific system. We choose the case of simultaneous particle (or electric) current and heat current flow. The interaction of these processes leads to the thermoelectric and thermo- and galvanomagnetic effects, and provides probably the most familiar example of the interaction of irreversible processes. Both Onsager and Casimir have made approximate applications of Reciprocal Relations to heat or particle current flow. The essential content of the methods used by these authors may be summarized in the following method of analysis:

a - The Method of Local Equilibrium

In order to apply Onsager's Relations to combined heat and electric current flow the conductor is, in this method, considered as a limiting case of a system composed of a series of segments each characterized by a definite value of the temperature and electrochemical potential. Within each segment the system is considered to be in local equilibrium. The actual system is considered to be the limiting case in which the length of the segments approach zero, and the temperature and electrochemical potential become continuous functions of position.

Because of the equilibrium assumed within each segment we can apply thermodynamics to the k^{th} segment, obtaining

$$\delta S_k = \frac{1}{T_k} \cdot \delta E_k - \left(\frac{\mu}{T}\right)_k \delta N_k \quad (11-1)$$

where S_k is the entropy of the segment

T_k is the temperature of the segment

E_k is the total internal energy of the segment

μ_k is the electro-chemical potential in the segment

N_k is the number of particles in the segment.

Now, consider the portion of a one-dimensional conductor included between the k^{th} and n^{th} segments. We consider that in the steady state energy flows into the k^{th} segment at the rate of $\frac{\delta E}{\delta t}$, and after traversing this portion of the conductor, this energy flows out of the n^{th} segment at the same rate. Similarly, the rate of flow of particles is $\frac{\delta N}{\delta t}$. Because the portion of the conductor $k \dots n$ is in a steady-state we are assured that its entropy is constant. The production of entropy which accompanies the irreversible process must occur in the systems which feed the k^{th} segment and which drain the n^{th} segment. These increases are, respectively

$$-\frac{1}{T_k} \frac{\delta E}{\delta t} + \left(\frac{\mu}{t}\right)_k \frac{\delta N}{\delta t}$$

and

$$+\frac{1}{T_n} \frac{\delta E}{\delta t} - \left(\frac{\mu}{t}\right)_n \frac{\delta N}{\delta t}$$

Thus, the total rate of increase of entropy associated with the flow in the portion of conductor $k \dots n$ is

$$\frac{\delta S_{k \dots n}}{\delta t} = \left(\frac{1}{T_n} - \frac{1}{T_k}\right) \frac{\delta E}{\delta t} - \left[\left(\frac{\mu}{T}\right)_n - \left(\frac{\mu}{T}\right)_k\right] \frac{\delta N}{\delta t} \quad (11-2)$$

Now, we let dx denote the distance between the k^{th} and n^{th} segments, and let the area of the conductor be A . Then

$$\frac{1}{T_n} = \frac{1}{T_k} + \nabla\left(\frac{1}{T}\right) \cdot dx \quad (11-3)$$

$$\left(\frac{\mu}{T}\right)_n = \left(\frac{\mu}{T}\right)_k + \nabla\left(\frac{\mu}{T}\right) \cdot dx$$

and

$$\frac{\delta}{\delta t} \left(\frac{S_{k \dots n}}{A dx} \right) = \nabla\left(\frac{1}{T}\right) \frac{\delta}{\delta t} \left(\frac{E}{A} \right) - \nabla\left(\frac{\mu}{T}\right) \frac{\delta}{\delta t} \left(\frac{N}{A} \right) \quad (11-4)$$

We now let

$$\frac{\delta}{\delta t} \left(\frac{S_{k 1 \dots n}}{A \delta x} \right) \equiv \dot{S}, \text{ the rate of increase of} \quad (11-5)$$

entropy associated with a unit volume of the system

$$\frac{\delta}{\delta t} \left(\frac{E}{A} \right) \equiv \vec{W}, \text{ the energy current density} \quad (11-6)$$

$$\frac{\delta}{\delta t} \left(\frac{N}{A} \right) \equiv \vec{J}, \text{ the particle current density} \quad (11-7)$$

Then (11-4) takes the form

$$\dot{S} = -\nabla \left(\frac{1}{T} \right) \vec{W} - \nabla \left(\frac{\mu}{T} \right) \vec{J} \quad (11-8)$$

and it is easily seen that this result follows in three dimensions as well as in one. It is thus reasoned that in analogy with (10-28), i.e.,

$$\frac{\delta S}{\delta t} = \gamma^{(1)} \frac{\delta \bar{x}^{(1)}}{\delta t} + \gamma^{(2)} \frac{\delta \bar{x}^{(2)}}{\delta t}$$

that $\nabla \frac{1}{T}$ and $\nabla \frac{\mu}{T}$ are the "forces" to be associated with the "currents" \vec{W} and $-\vec{J}$. Then Onsager's Relations give, in the absence of a magnetic field,

$$-\vec{J} = L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} \quad (11-9)$$

$$\vec{W} = L'_{12} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T}$$

where the quantities L'_{jk} are "kinetic coefficients". There is a certain arbitrariness here, connected with the fact that only $\nabla \cdot \vec{W}$ is physically defined. For a discussion of this difficulty we refer to Casimir.

The point at which an approximation is made in this treatment is in the initial assumption that the conductor may be considered as the limiting case of a series of segments each in local equilibrium. Early in the development of the free-electron theory of conductivity in metals the attempt was made to attribute to the electrons a distribution function which was identical to the equilibrium distribution function except that the parameters μ and T were assumed to depend on x . It is clear that this is equivalent to the assumption made above. However, it is well-known that such a simple form for the distribution function was not successful. Boltzmann was aware of the inadequacy of such a distribution function, and the Boltzmann kinetic equation gives an approximate method of evaluation of the deviation of the distribution function in the steady-state from its equilibrium value. Both Lorentz and Sommerfeld have analyzed the conductivity in metals on the basis of the Boltzmann kinetic equation, employing Maxwell-Boltzmann and Fermi-Dirac statistics respectively. By these methods the deviation of the distribution function from the local-equilibrium value is treated as a small perturbation, and because of the smallness of this deviation we expect the application of Onsager's Relations to steady-state processes to be a very good approximation. However, it is interesting to utilize the Sommerfeld theory of conductivity to investigate this approximation further. In this way we shall find that the application of Onsager's Relations represents an approximation which is just as valid as is the macroscopic linear kinetic law (Ohm's Law) which governs the process.

b - The Sommerfeld Free-Electron Theory, and Onsager's Relations

The general method of investigation of the effect of a deviation of the true distribution function from the "local-equilibrium" value is clear. If we express the coarse-grain density vector as

$$\vec{\rho} = \vec{\rho}^0 + \vec{\rho}' \quad (11-10)$$

where $\vec{\rho}^0$ is the value which it would have if the system were the limiting case of segments each in local equilibrium

and $\vec{\rho}'$ is a small deviation.

$$\text{Then} \quad \delta S = -k \sum_j \ln \rho_j \cdot \delta \rho_j \quad (11-11)$$

$$= -k \sum_j \ln(\rho_j^0 + \rho_j') \cdot \delta \rho_j$$

$$= -k \sum_j \ln \rho_j^0 \cdot \delta \rho_j - k \sum_j \frac{\rho_j'}{\rho_j^0} \delta \rho_j + \dots \quad (11-12)$$

$$= \delta S^0 - k \sum_j \frac{\rho_j'}{\rho_j^0} \delta \rho_j + \dots \quad (11-13)$$

Thus we see that δS is obtained as the "local-equilibrium" value,

$$\delta S^0 = \frac{1}{T} \delta E - \frac{\mu}{T} \delta N, \text{ plus a small correction } -k \sum_j \frac{\rho_j'}{\rho_j^0} \delta \rho_j. \text{ If we know}$$

ρ_j' we can calculate this correction in terms of macroscopic quantities, and the logic following (11-1) above will then be altered in accordance with this correction term, leading to a slightly different form for the final kinetic equations (11-9). It should be stressed that we do not expect to obtain a change of the kinetic equations which has practical significance - certainly the physically significant form of these equations is that which is obtained by the "method of local equilibrium". The value

of the present calculation is to be viewed only as giving insight into the approximation underlying the practical form (11-9) of the kinetic equations.

In order to obtain an expression for δS in terms of the free-electron theory we shall not find it convenient to use a formalism quite like that indicated in (11-2), but because of the character of the system considered it is convenient to carry out the calculation in the μ -space of Maxwell rather than in the Γ -space of Gibbs. Each micro-state of the electron gas is then represented by N points in the μ -space, where N is the total number of electrons. The μ -space is considered to be divided up into many regions, each region containing many "cells". A cell is the volume of the μ -space which corresponds to a single micro-state for a single electron - and the Fermi-Dirac statistics demands that there may be only one electron per cell. Then the gas is characterized by giving for all j the fraction f_j of the g_j cells in the j^{th} region which are occupied by electrons. The entropy to be associated with such a specification of state is

$$S = -k \sum_j g_j [f_j \ln f_j + (1 - f_j) \ln (1 - f_j)] \quad (11-14)$$

whence

$$\delta S = -k \sum_j g_j \ln \frac{f_j}{1 - f_j} \delta f_j \quad (11-15)$$

For the free-electron gas the regions in μ -space may be taken as energy shells, and

$$g_j \rightarrow g(\epsilon) d\epsilon = \frac{m^3}{h^3} V dv_x dv_y dv_z \quad (11-16)$$

In equilibrium, the maximization of (11-14) gives

$$f_j^0 = \frac{1}{e^{\frac{\epsilon_j - \mu}{kT}} + 1} \quad (11-17)$$

where ϵ_j is the energy of an electron, and μ is the electro-chemical potential. Following Sommerfeld we now put

$$f_j = f_j^0 + v_{xj} \phi_j \quad (11-18)$$

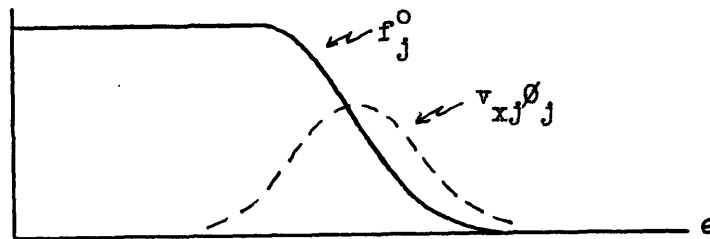
where ϕ_j depends only on $v^2 = v_x^2 + v_y^2 + v_z^2$, and

$$\text{where } v_{xj} \phi_j \ll f_j^0 \quad (11-19)$$

In addition we will assume that

$$v_{xj} \phi_j \ll (1 - f_j^0) \quad (11-20)$$

These two restrictions on the magnitude of $v_{xj} \phi_j$ require that $v_{xj} \phi_j \rightarrow 0$ when either $f_j^0 \rightarrow 0$ or $f_j^0 \rightarrow 1$, so that only electrons in the sloping portion of the Fermi distribution suffer appreciable deviation of their f_j from the equilibrium value.



Substituting $f_j = f_j^0 + v_{xj} \phi_j$ in our expression (11-15) for δS , and neglecting higher powers of $\frac{v_{xj} \phi_j}{f_j^0}$ we obtain

$$\delta S = -k \sum_j g_j \ln \frac{f_j^0}{1 - f_j^0} - k \sum_j g_j \frac{v_{xj} \phi_j}{f_j^0 (1 - f_j^0)} \delta f_j \quad (11-21)$$

If we now insert the value (11-17) for f_j^0 into the first summation we find

$$\delta S = \left[\frac{1}{T} \delta E - \frac{\mu}{T} \delta N \right] - k \sum_j g_j \frac{v_{xj} \phi_j}{f_j^0 (1 - f_j^0)} \delta f_j \quad (11-22)$$

or
$$\delta S = \delta S^0 + \delta S' \quad (11-23)$$

We now wish to express the small correction term $\delta S'$ in terms of macroscopic quantities. The function $\phi_j(v)$ is determined by the application of the Boltzmann kinetic equation and one obtains (cf. Sommerfeld)

$$\phi_j = - \frac{l_j}{v_j} \left(\frac{\delta f_j^0}{\delta x} + \nabla_{x\mu} \frac{\delta f_j^0}{\delta \epsilon_j} \right) \quad (11-24)$$

where l_j is the mean free path between collisions. Thus $\delta S'$ becomes

$$\begin{aligned} \delta S' &= k \sum_j g_j v_{xj} \frac{1}{f_j^0 (1 - f_j^0)} \frac{l_j}{v_j} \left(\frac{\delta f_j^0}{\delta x} + \nabla_{x\mu} \frac{\delta f_j^0}{\delta \epsilon_j} \right) \delta f_j \\ &= k \sum_j g_j v_{xj} \frac{l_j}{v_j} \left(\frac{\delta}{\delta x} + \nabla_{x\mu} \frac{\delta}{\delta \epsilon_j} \right) \ln \frac{f_j^0}{1 - f_j^0} \cdot \delta f_j \end{aligned} \quad (11-25)$$

But taking the value of f_j^0 from (11-17),

$$\ln \frac{f_j^0}{1 - f_j^0} = - \frac{\epsilon_j - \mu}{kT}$$

and inserting this in (11-25)

$$\delta S' = \sum_j g_j v_{xj} \frac{l_j}{v_j} (\mu - \epsilon_j) \nabla_x \left(\frac{1}{T} \right) \cdot \delta f_j \quad (11-26)$$

The quantity $v_{xj} l_j / v_j$ may be recognized as the mean x-displacement per collision, which we denote by l_{jx} :

$$\delta S' = \nabla_x \frac{1}{T} \sum_j g_j l_{jx} (\mu - \epsilon_j) \cdot \delta f_j \quad (11-27)$$

$$\text{or} \quad \delta S = \frac{1}{T} \delta E - \frac{\mu}{T} \delta N + \nabla \frac{1}{T} \cdot \delta(\overline{l(\mu - \epsilon)}) \quad (11-28)$$

where $\overline{l(\mu - \epsilon)}$ is the mean product of free path and $(\mu - \epsilon)$.

If we now consider a steady-state process, just as in part "a" above, we obtain

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{W} - \nabla \frac{\mu}{T} \cdot \vec{J} + \nabla^2 \frac{1}{T} \cdot \overrightarrow{l(\mu - \epsilon)} \quad (11-29)$$

where $\overrightarrow{l(\mu - \epsilon)}$ is the flow, or current, to be associated with $\overline{l(\mu - \epsilon)}$.

This current is certainly not familiar, but its meaning is clear. Thus, when an electron leaves a region it will change the mean value of the quantity $l(\mu - \epsilon)$ in the region which it has left, and the rate of change of this quantity is the value of $\overrightarrow{l(\mu - \epsilon)}$ to be associated with the flow of that electron. It is perhaps well, in light of the peculiar nature of this current, to reemphasize here that we do not intend to propose this current for any practical application, but we introduce it here only temporarily in order to establish a criterion for the validity of the approximation involved when it is neglected.

In the light of (11-29) we are now able to identify the proper currents and the corresponding forces, and invoking the Reciprocal Relations:

$$\begin{aligned} -\vec{J} &= L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} + L'_{13} \nabla^2 \frac{1}{T} \\ \vec{W} &= L'_{12} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T} + L'_{23} \nabla^2 \frac{1}{T} \\ \overrightarrow{l(\mu - \epsilon)} &= L'_{13} \nabla \frac{\mu}{T} + L'_{23} \nabla \frac{1}{T} + L'_{33} \nabla^2 \frac{1}{T} \end{aligned} \quad (11-30)$$

Now we are provided with a simple empirical test for the approximation which we wish to make. Only the first two equations above are physically interesting, and in order that they may be written in the form

$$-\vec{J} = L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} \quad (11-31)$$

$$\vec{W} = L'_{12} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T}$$

we must have $L'_{13}/L'_{11} \ll 1$, etc. (11-32)

In practical applications this, of course, is true and it is found that the kinetic equations satisfactorily account for the observed phenomena if they are written in the simple form (11-31) without the inclusion of the higher derivatives appearing in (11-30). To the same approximation (11-29) becomes

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{W} - \nabla \frac{\mu}{T} \cdot \vec{J} \quad (11-33)$$

just as we found in part "a" above.

Thus we finally see that the simple method of application of Onsager's Relations based on the assumption of local equilibrium is justified by the empirical fact that the kinetic equations may be written satisfactorily in terms of the first derivatives, $\nabla \frac{1}{T}$ and $\nabla \frac{\mu}{T}$, alone.

c - The Quasi-Thermodynamic Method of Kelvin

In 1854 Lord Kelvin (then Sir W. Thomson) made a theoretical analysis of the thermoelectric effects which accompany the simultaneous flow of electric and heat currents. The result of this analysis was a set of relations among the effects; these relations are equivalent, as we shall

see in the following Sections, to the symmetry of the kinetic equations (11-31) as predicted also by Onsager's Relations. The quasi-thermodynamic method developed by Kelvin has been widely exploited to give the equivalent of Reciprocal Relations in several types of processes. Thus Bridgman has studied thermomagnetic and galvanomagnetic effects, Helmholtz has studied the interaction of diffusion and electric current flow in electrolytic cells, and Eastman has studied the interaction of diffusion and heat current flow (Soret effect). However, Kelvin himself felt that his quasi-thermodynamic argument was only suggestive rather than rigorous, and he stressed the desirability of experimental justification of conclusions drawn from it. In the intervening years the conclusions drawn from this type of argument in the several fields mentioned above have been so notably successful that great confidence in the method has developed, and much attention has been paid to the theoretical justification of it. We are now in a position to inquire into the nature of Kelvin's assumption.

In Kelvin's method of analysis of the thermoelectric effects the electric current and the temperature gradient in a system are considered to be experimentally controlled and known. Then, although the thermoelectric effects imply a certain interference between the electric and heat currents, the Kelvin assumption is that the total entropy production is due to just two independent causes; 1) the Joule heating, independent of the temperature gradient, and 2) the entropy production which would be associated with the temperature gradient in the absence of an electric current. Now, if we use the

kinetic equations (11-9) to express the entropy production in terms of \vec{J} and $\nabla \frac{1}{T}$ we do, in fact, find just such a division into two independent causes of entropy production;

$$\dot{S} = \frac{1}{L'_{11}} J^2 + \frac{L'_{11}L'_{22} - L'^2_{12}}{L'_{11}} \left(\nabla \frac{1}{T} \right)^2 \quad (11-34)$$

and the absence of additional terms involving $\vec{J} \cdot \nabla \frac{1}{T}$ is a result of the symmetry relation $L'_{12} = L'_{21}$. Thus, Kelvin's assumption in the form (11-34), plus the adoption of the local equilibrium equation (11-33) for \dot{S} , is equivalent to the assumption of the Onsager symmetry relation.

Because the thermoelectric effects imply no production of entropy other than that due to the two causes discussed above, the effects are sometimes termed "reversible". This terminology must, however, be regarded as no more than a mere figure of speech. In actuality, only a process, and not an effect, may properly be spoken of as being either reversible or irreversible - and the flow of electric and heat currents in resistive media is inseparably associated with a production of entropy and must be considered as essentially irreversible.

12 - Thermoelectric Effects

The very great practical importance and wide application of the thermocouple as a temperature measuring instrument has resulted in the thermoelectric effects being the most familiar examples of coupled irreversible processes. The application of the quasi-thermodynamic type of argument has led to the important Kelvin Relations connecting the various effects (cf. Kelvin), and the effects have also been extensively studied in terms of particular models. Thus Bohr has studied the effects on the basis of a classical model, Sommerfeld and Frank have studied the effects on the basis of the free-electron theory, Wilson has studied the effects in semi-conductors, and Meixner has studied the effects in metals. In addition, as we have seen in the preceding Section, Onsager's Relations may be applied to the simultaneous flow of electricity and heat; and the symmetry of the kinetic equations so obtained is, as pointed out by Onsager, equivalent to the Kelvin Relations. The "method of local equilibrium", upon which the application of Onsager's Relations is based, provides us with an interesting formulation of the thermoelectric effects in terms of entropy current, and we shall consider this formulation in this Section.

We have seen in the preceding Section that the method of local equilibrium, applied to the simultaneous flow of electric and heat currents, gives

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{W} - \nabla \frac{\mu}{T} \cdot \vec{J} \quad (12-1)$$

where

\dot{S} is the rate of production of entropy associated with unit volume of the system.

T is the absolute temperature.

\vec{W} is the energy current density. The divergence of \vec{W} is the rate of change of thermodynamic internal energy per unit volume.

\vec{J} is the particle current density. The electric current density is $e\vec{J}$, where e is the electronic charge, and we use the terms particle current and electric current virtually interchangeably. The divergence of \vec{J} is the rate of change of particle density.

μ is the electro-chemical potential, which may be considered as the sum of an electrostatic and a chemical potential:

$$\mu \equiv \mu_c + \mu_e$$

where

μ_c is the chemical potential per particle

μ_e is the electrostatic potential energy per particle

An entropy current density may be defined. In accordance with the thermodynamic equation

$$\delta S = \frac{1}{T} \delta E - \frac{\mu}{T} \delta N \quad (12-2)$$

we define the entropy current density by

$$\vec{S} = \frac{1}{T} \vec{W} - \frac{\mu}{T} \vec{J} \quad (12-3)$$

We note that in the steady-state

$$\nabla \cdot \vec{W} = \nabla \cdot \vec{J} = 0 \quad (12-4)$$

and
$$\nabla \cdot \vec{S} = \nabla \cdot \frac{1}{T} \cdot \vec{W} - \nabla \cdot \frac{\mu}{T} \cdot \vec{J} = \dot{S} \quad (12-5)$$

which is simply the equation of continuity for the entropy. Several authors have considered an entropy current of this type (cf. Herring; Leaf).

We shall find it useful also to define a heat current density. Although several quantities have been referred to as "heat current" in the literature (cf. Onsager II, p. 2268; Sommerfeld and Frank; Leaf) it seems to us that the most satisfactory and generally consistent definition is, in analogy with $\delta Q = T \delta S$:

$$\vec{Q} \equiv T \vec{S} \quad (12-6)$$

$$= \vec{W} - \mu \vec{J} \quad (12-7)$$

This latter equation may be viewed as defining the flux of heat as the difference between the total energy flux and the "electro-chemical energy" flux. This agrees with our intuitive notion of heat being a kind of kinetic energy and the electro-chemical energy being a kind of potential-energy, the sum of the two being the total energy. It is perhaps well to note here that the "heat current" introduced by Sommerfeld and Frank and defined by $\sum_{\text{electrons}} \vec{v} \left(\frac{1}{2} m v^2\right)$ is, in our notation,

$$\text{equal to } \vec{W} - \mu_e \vec{J} = \vec{Q} + \mu_c \vec{J}.$$

Unlike \vec{W} and \vec{J} , the heat current density is not divergenceless in the steady-state. In fact, taking the divergence of (12-7):

$$\nabla \cdot \vec{Q} = - \nabla \mu \cdot \vec{J} \quad (12-8)$$

This equation expresses the "degradation" of electro-chemical energy into heat energy as the particles flow from regions of high electro-chemical potential to low.

The rate of production of entropy can be written in terms of \vec{Q} and \vec{J} rather than \vec{W} and \vec{J} by replacing \vec{W} by $\vec{Q} + \mu \vec{J}$ in (12-1):

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{Q} - \frac{1}{T} \nabla \mu \cdot \vec{J} \quad (12-9)$$

Combining this expression with (12-8) we may also write the entropy production as

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{Q} + \frac{1}{T} \nabla \cdot \vec{Q} \quad (12-10)$$

which states that the increase in entropy arises from two causes; the first term is the increase in entropy due to the flow of heat from high to low temperature, and the second term is the increase in entropy due to the degradation of electro-chemical energy into heat energy.

The two equations (12-1) and (12-9) for \dot{S} in terms of \vec{J} and \vec{W} , and in terms of \vec{J} and \vec{Q} , provide us with two ways to choose proper currents and forces for the application of Onsager's Relations. Accordingly, we can write, in the absence of a magnetic field:

$$\begin{cases} -\vec{J} = L'_{11} \nabla \frac{\mu}{T} + L'_{12} \nabla \frac{1}{T} \\ \vec{W} = L'_{12} \nabla \frac{\mu}{T} + L'_{22} \nabla \frac{1}{T} \end{cases} \quad (12-10)$$

or,

$$\begin{cases} -\vec{J} = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \\ \vec{Q} = L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T} \end{cases} \quad (12-11)$$

We shall find it convenient in our analysis of the thermoelectric effects to utilize the second, or unprimed, set of kinetic coefficients. The relations between the two sets of kinetic coefficients may be easily obtained by using equation (12-7).

The kinetic coefficients are properties of the medium considered, and are closely related to such familiar properties as the electrical and heat conductivities. We shall see that the set of quantities L_{11} , L_{12} , and L_{22} is equivalent to the knowledge of the electrical and heat conductivities and of the thermoelectric power of the medium.

The heat conductivity is defined as the heat current density per unit temperature gradient, for zero particle current.

$$\kappa \equiv - \vec{Q} / \nabla T \quad \text{for } \vec{J} = 0 \quad (12-12)$$

To obtain κ in terms of the kinetic coefficients we put $\vec{J} = 0$ in (12-11), and eliminate $\frac{1}{T} \nabla \mu$ between the two equations, obtaining

$$\begin{aligned} \vec{Q} &= + \frac{D}{L_{11}} \nabla \frac{1}{T} \\ &= - \frac{1}{T^2} \frac{D}{L_{11}} \nabla T \end{aligned}$$

where $D \equiv L_{11}L_{22} - L_{12}^2 \quad (12-13)$

Thus $\kappa = + \frac{1}{T^2} \frac{D}{L_{11}} \quad (12-14)$

Similarly, the electric conductivity is defined as the electric current density ($e \vec{J}$) per unit potential gradient ($\nabla \frac{\mu}{e}$) in an isothermal system: It is easily seen that $\nabla \frac{\mu}{e}$ is truly the electrostatic emf., for μ may be considered as the sum of an electrostatic potential energy per particle μ_e and of a chemical potential energy per particle μ_c . But μ_c depends only on T ,* and if $\nabla T = 0$ then $\nabla \mu_c = 0$ and $\nabla \mu = \nabla \mu_e$. Thus, in an isothermal system $\nabla \frac{\mu}{e}$ is the electrostatic emf., and

$$\sigma = - e \vec{J} / \nabla \frac{\mu}{e} \quad \text{for } \nabla T = 0 \quad (12-15)$$

* (considering the medium to be homogeneous)

The first equation (12-11) immediately gives

$$\sigma = \frac{e^2}{T} L_{11} \quad (12-16)$$

In preparation for our application of the kinetic equations to practical experiments we note that the variables which can most easily be independently controlled by the experimenter are the particle (or electric) current density and the temperature gradient. We therefore find it convenient to express \vec{S} in terms of these variables. Eliminating $\frac{1}{T} \nabla \mu$ between our two kinetic equations (12-11) we obtain

$$L_{11} \vec{Q} + L_{12} \vec{J} = D \nabla \frac{1}{T}$$

whence
$$\vec{S} \equiv \frac{1}{T} \vec{Q} = - \frac{L_{12}}{TL_{11}} \vec{J} + \frac{D}{TL_{11}} \nabla \frac{1}{T} \quad (12-17)$$

According to this equation a current flowing in a conductor of given fixed temperature distribution carries with it an entropy per particle of $-\frac{L_{12}}{TL_{11}}$. This entropy flow is, of course, in addition to the entropy flow $\frac{D}{TL_{11}} \nabla \frac{1}{T}$, which is independent of the particle current. The entropy flow per particle $\frac{L_{12}}{TL_{11}}$ will prove to be such a useful quantity in our study of the thermoelectric effects that we introduce for it the special symbol S_J

$$S_J \equiv - \frac{L_{12}}{TL_{11}} \quad (12-18)$$

We shall see, in our investigation of thermoelectric effects, that S_J/e ($e =$ electronic charge) is equal to the thermoelectric power of the substance considered, so that, like κ and σ , it has direct physical significance as a property of the substance. The three kinetic coefficients L_{11} , L_{12} and L_{22} may be expressed in terms of the three quantities κ , σ ,

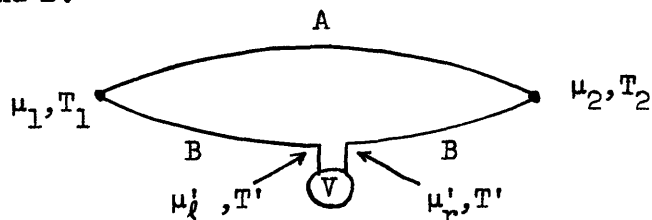
and S_J , or vice versa. The kinetic entropy per particle S_J was introduced by C. Herring, who also showed its relation to the coefficient of the Thomson effect.

We now consider the various thermoelectric effects in turn.

a - The Seebeck Effect

The Seebeck effect refers to the production of an electromotive force in a thermocouple, under conditions of zero electrical current.

Consider a thermocouple with junctions at temperatures T_1 and T_2 ($T_2 > T_1$). Let the thermocouple be broken at a point at which the temperature is T' and let a voltmeter be inserted. This voltmeter is to be one which allows no passage of electricity but which offers no resistance to the flow of heat. We designate the two materials composing the thermocouple by A and B.



In conductor A we have the kinetic equations

$$-\vec{J} = L_{11}^A \frac{1}{T} \nabla \mu + L_{12}^A \nabla \frac{1}{T} \quad (12-19)$$

$$\vec{Q} = L_{12}^A \frac{1}{T} \nabla \mu + L_{22}^A \nabla \frac{1}{T}$$

and since $\vec{J} = 0$ the first of these equations gives

$$\nabla \mu = \frac{L_{12}^A}{T L_{11}^A} \nabla T$$

$$\text{or} \quad \nabla \mu = -S_J^A \cdot \nabla T \quad (12-20)$$

(It is interesting to note the formal similarity of this equation to the thermodynamic equation $\frac{d\mu_c}{dT} = -S$). We now assume $T_2 - T_1$ and $\mu_2 - \mu_1$ to be very small so that we can use mean values for the L's or for S_J , and write

$$\mu_2 - \mu_1 = -S_J^A (T_2 - T_1) \quad (12-21)$$

Similarly, in the other conductor

$$\mu_2 - \mu_r' = -S_J^B (T_2 - T') \quad (12-22)$$

and
$$\mu_r' - \mu_1 = -S_J^B (T' - T_1) \quad (12-23)$$

Eliminating μ_1 and μ_2 from these three equations

$$\mu_r' - \mu_r' = (S_J^B - S_J^A) (T_2 - T_1) \quad (12-24)$$

We now note that μ_c must have the same value on either side of the voltmeter because the temperatures at these two points are the same. Thus $\mu_r' - \mu_r'$ is simply the difference of the electrostatic potential energy per particle, and the reading of the voltmeter is $V = \frac{1}{e} (\mu_r' - \mu_r')$, where e is the charge per particle.

or
$$V = \frac{1}{e} (S_J^B - S_J^A) (T_2 - T_1) \quad (12-25)$$

The Seebeck coefficient, or the thermoelectric power of the thermocouple, \mathcal{E}_{AB} , is defined as the voltage per unit temperature difference. The sign of \mathcal{E}_{AB} is chosen as positive if the voltage is such as to drive the current from A to B at the hot junction. Then

$$\mathcal{E}_{AB} \equiv \frac{V}{T_2 - T_1} = \frac{1}{e} (S_J^B - S_J^A) \quad (12-26)$$

The quantities $\frac{1}{e} S_J^B$ and $\frac{1}{e} S_J^A$ are referred to as the thermoelectric powers of materials A and B. Thus the entropy flow per particle S_J has a direct significance as a physical property of the material.

b - The Peltier Effect

The Peltier effect refers to the evolution of heat accompanying the flow of an electric current across an isothermal junction of two materials.

Consider an isothermal junction of two conductors A and B, and consider a current \vec{J} to be flowing. Then the total energy flow will be discontinuous across the junction, and the energy difference appears as "Peltier heat" at the junction.



We have $\vec{W} = \vec{Q} + \mu\vec{J}$, and since both μ and \vec{J} are continuous across the junction

$$\vec{W}_B - \vec{W}_A = \vec{Q}_B - \vec{Q}_A \quad (12-27)$$

In either conductor we have

$$-\vec{J} = L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T}$$

$$\vec{Q} = L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T}$$

and putting $\nabla \frac{1}{T} = 0$, and eliminating $\frac{1}{T} \nabla \mu$ between these two equations we obtain

$$\vec{Q} = - \frac{L_{12}}{L_{11}} \vec{J} = T S_J \vec{J} \quad (12-28)$$

Thus

$$\vec{Q}_B - \vec{Q}_A = T(S_J^B - S_J^A) \vec{J} \quad (12-29)$$

the Peltier coefficient π_{AB} is defined as the heat which must be supplied to the junction when unit electric current passes from conductor A to conductor B. Since the electrical current density is $e \vec{J}$, the Peltier coefficient is

$$\pi_{AB} = \frac{Q_B - Q_A}{e J} = \frac{T}{e} (S_J^B - S_J^A) \quad (12-30)$$

The Peltier coefficient has the dimensions of an electromotive force, and is sometimes referred to as the Peltier emf. This terminology must, however, be viewed as a mere figure of speech, for the potential μ is actually continuous at the junction.

We may regard the Peltier heat as supplying the discontinuity in the entropy flow per particle at the junction. For by (12-29)

$$\vec{S}_B - \vec{S}_A = (S_J^B - S_J^A) \vec{J} \quad (12-31)$$

so that a "Peltier entropy" must be supplied to the junction, and this Peltier entropy is $\frac{1}{T} \pi$ (Peltier Heat).

c - The Thomson Effect

The Thomson effect refers to the evolution of heat as an electric current traverses a temperature gradient in a material. Because it is the only one of the three thermoelectric effects which deals with a single material it is sometimes called "the homogeneous thermoelectric effect".

Consider a conductor carrying a heat current, but no electric current. A temperature distribution governed by the temperature dependence of the kinetic coefficients will be set up. Let the conductor

be placed in contact at each point with a heat reservoir of the same temperature as that point, so that there is no heat interchange between conductor and reservoirs. Now, let an electric current pass through the conductor. Then a heat interchange will take place between conductor and reservoirs, this heat consisting of two parts - the Joule heat and the Thomson heat.

As the electric current passes along the conductor any change in total energy flow must be supplied by an energy interchange with the reservoirs. Thus, we must compute $\nabla \cdot \vec{W}$.

$$\nabla \cdot \vec{W} = \nabla \cdot (\vec{Q} + \mu \vec{J}) = \nabla \cdot \vec{Q} + \nabla \mu \cdot \vec{J} \quad (12-32)$$

The kinetic equations can be put in the form

$$\begin{aligned} \nabla \mu &= - \frac{T}{L_{11}} \cdot \vec{J} - \frac{TL_{12}}{L_{11}} \nabla \frac{1}{T} \\ \vec{Q} &= - \frac{L_{12}}{L_{11}} \vec{J} - \frac{D}{L_{11}} \nabla \frac{1}{T} \end{aligned} \quad (12-33)$$

whence

$$\nabla \cdot \vec{W} = - \nabla \cdot \left(\frac{L_{12}}{L_{11}} \vec{J} - \nabla \cdot \left(\frac{D}{L_{11}} \nabla \frac{1}{T} \right) - \frac{T}{L_{11}} J^2 - \frac{T L_{12}}{L_{11}} \vec{J} \cdot \nabla \frac{1}{T} \right) \quad (12-34)$$

We must now recall that the temperature distribution is that which is determined by the steady-state with no electric current. If $\vec{J}=0$ then the second of equations (12-33) gives

$$\nabla \cdot \vec{Q} = - \nabla \cdot \left(\frac{D}{L_{11}} \nabla \frac{1}{T} \right) = 0 \quad (12-35)$$

where we put $\nabla \cdot \vec{Q} = 0$ because when $\vec{J} = 0$ then $\vec{Q} = \vec{W}$, which must be divergenceless. When the electric current is allowed to flow the distribution in temperature is maintained constant although the distribution in μ changes. But the kinetic coefficients depend only on T and not on μ

(this is apparent, since the zero of μ is arbitrary, whereas the L 's are uniquely defined). Thus the kinetic coefficients, as well as the temperature distribution, remain constant when the electric current is allowed to flow. We may thus put

$$\nabla \cdot \left(\frac{D}{L_{11}} \nabla \frac{1}{T} \right) = 0 \quad (12-36)$$

in equation (12-34) obtaining

$$\nabla \cdot \vec{W} = -\nabla \left(\frac{L_{12}}{L_{11}} \right) \cdot \vec{J} - \frac{T}{L_{11}} J^2 - \frac{\pi L_{12}}{L_{11}} \vec{J} \cdot \nabla \frac{1}{T} \quad (12-37)$$

$$\begin{aligned} \nabla \cdot \vec{W} &= -\frac{T}{L_{11}} J^2 - \frac{\delta}{\delta T} \left(\frac{L_{12}}{L_{11}} \right) \nabla T \cdot \vec{J} + \frac{L_{12}}{\pi L_{11}} \nabla T \cdot \vec{J} \\ &= -\frac{T}{L_{11}} J^2 - T \frac{\delta}{\delta T} \left(\frac{L_{12}}{\pi L_{11}} \right) \nabla T \cdot \vec{J} \\ &= -\frac{T}{L_{11}} J^2 + T \frac{\delta S_J}{\delta T} \nabla T \cdot \vec{J} \end{aligned} \quad (12-38)$$

Since, by (12-16), the electrical conductivity is $\sigma = e^2 \frac{L_{11}}{T}$ we

recognize the first term above as the Joule heat. The second term therefore gives the Thomson heat. The Thomson coefficient τ is defined as the ratio of the Thomson heat absorbed to the product $\nabla T \cdot \vec{J} e$

$$\tau \equiv \frac{\text{Thomson heat}}{\nabla T \cdot \vec{J} e} = \frac{T}{e} \frac{\delta S_J}{\delta T} \quad (12-39)$$

It will be noted that the form of this equation suggests the analogy of

τ to a specific heat $\left(= T \frac{\delta S}{\delta T} \right)$, and, in fact, Thomson referred to τ as the "specific heat of electricity".

The details of the entropy transfer between conductor and reservoirs gives an interesting insight into the Thomson effect. Because of the condition (12-36) one obtains

$$\nabla \cdot \vec{S} = +\nabla s_J \cdot \vec{J} + \frac{D}{L_{11}} \left(\nabla \frac{1}{T} \right)^2 \quad (12-40)$$

and

$$\dot{s} = \frac{1}{L_{11}} J^2 + \frac{D}{L_{11}} \left(\nabla \frac{1}{T} \right)^2 \quad (12-41)$$

Thus the reservoirs must provide an input of entropy given by

$$\nabla \cdot \vec{S} - \dot{s} = -\frac{1}{L_{11}} J^2 + \nabla s_J \cdot \vec{J} \quad (12-42)$$

which represents a Joule and a Thomson contribution. The Joule contribution extracts the entropy produced by the flow of current (12-41), and the Thomson contribution injects entropy to supply the flow of entropy per particle s_J , (12-40).

d - The Kelvin Relations

The Kelvin Relations connect the three thermoelectric coefficients. Recalling our values (12-26), (12-30), and (12-39) for these coefficients:

$$\text{Seebeck coefficient: } \mathcal{E}_{AB} = \frac{1}{e} (s_J^B - s_J^A)$$

$$\text{Peltier coefficient: } \pi_{AB} = \frac{T}{e} (s_J^B - s_J^A)$$

$$\text{Thomson coefficient: } \tau = \frac{T}{e} \frac{\delta s_J}{\delta T}$$

we immediately obtain the Kelvin Relations

$$\left\{ \begin{array}{l} \pi_{AB} = T \mathcal{E}_{AB} \\ \tau_B - \tau_A = T \frac{d\mathcal{E}_{AB}}{dT} \end{array} \right. \quad (12-43)$$

13 - The Thermo- and Galvanomagnetic Effects

If a magnetic field is applied to the system discussed in the preceding Section several new effects appear. These effects have been studied by Bridgman and by Lorentz on the basis of the quasi-thermodynamic method. In addition Onsager has stated that the Reciprocal Relations imply a relation, due to Bridgman, between the Nernst and Ettinghausen effects. As an illustration of the application of the Onsager Relations in a magnetic field we shall consider the thermo- and galvanomagnetic effects in this Section.

We consider that the flow of heat and electric currents is confined to the x-y plane. Then only the z-component of the magnetic field is effective, and for simplicity we consider that the magnetic field is along the z-axis.

As in the preceding Section, we can define a heat current density \vec{Q} , and an entropy current density \vec{S} :

$$\vec{S} \equiv \frac{1}{T} \vec{W} - \frac{\mu}{T} \vec{J} \quad (13-1)$$

$$\vec{Q} \equiv T \vec{S} = \vec{W} - \mu \vec{J} \quad (13-2)$$

and again we have

$$\dot{S} = \nabla \cdot \frac{1}{T} \vec{Q} - \frac{1}{T} \nabla \mu \cdot \vec{J} \quad (13-3)$$

or, written in component form,

$$\dot{S} = \nabla_x \cdot \frac{1}{T} \vec{Q}_x + \nabla_y \cdot \frac{1}{T} \vec{Q}_y - \frac{1}{T} \nabla_x \mu \cdot J_x - \frac{1}{T} \nabla_y \mu \cdot J_y \quad (13-4)$$

This expression for \dot{S} allows us to identify proper currents and forces for the application of Onsager's Relations. Thus

$$\begin{aligned}
 -J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T} \\
 Q_x &= L_{21} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{23} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T} \\
 -J_y &= L_{31} \frac{1}{T} \nabla_x \mu + L_{32} \nabla_x \frac{1}{T} + L_{33} \frac{1}{T} \nabla_y \mu + L_{34} \nabla_y \frac{1}{T} \\
 Q_y &= L_{41} \frac{1}{T} \nabla_x \mu + L_{42} \nabla_x \frac{1}{T} + L_{43} \frac{1}{T} \nabla_y \mu + L_{44} \nabla_y \frac{1}{T}
 \end{aligned} \tag{13-5}$$

These equations must be invariant with respect to a rotation of the axes through an angle of 90° around the z-axis. That is, they must be invariant with respect to the transformation

$$x \rightarrow -y \qquad y \rightarrow +x \qquad z \rightarrow +z \tag{13-6}$$

Making this transformation substitution in (13-5) we find certain symmetries among the kinetic coefficients, so that we may now write (13-5) in the form:

$$\begin{aligned}
 -J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T} \\
 Q_x &= L_{21} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{23} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T} \\
 -J_y &= -L_{13} \frac{1}{T} \nabla_x \mu - L_{14} \nabla_x \frac{1}{T} + L_{11} \frac{1}{T} \nabla_y \mu + L_{12} \nabla_y \frac{1}{T} \\
 Q_y &= -L_{23} \frac{1}{T} \nabla_x \mu - L_{24} \nabla_x \frac{1}{T} + L_{21} \frac{1}{T} \nabla_y \mu + L_{22} \nabla_y \frac{1}{T}
 \end{aligned} \tag{13-7}$$

Similarly, the kinetic equations must be invariant with respect to a rotation of the axes through 180° around the x-axis, or to the transformation

$$x \rightarrow x \qquad y \rightarrow -y \qquad z \rightarrow -z \tag{13-8}$$

The transformation $z \rightarrow -z$ is equivalent to $A \rightarrow -A$, where A is the magnetic vector potential. Making the substitution (13-8) in (13-7) we obtain

$$\begin{aligned}
 -J_x &= L_{11}(-A) \frac{1}{T} \nabla_x \mu + L_{12}(-A) \nabla_x \frac{1}{T} - L_{13}(-A) \frac{1}{T} \nabla_y \mu - L_{14}(-A) \nabla_y \frac{1}{T} \\
 Q_x &= L_{21}(-A) \frac{1}{T} \nabla_x \mu + L_{22}(-A) \nabla_x \frac{1}{T} - L_{23}(-A) \frac{1}{T} \nabla_y \mu - L_{24}(-A) \nabla_y \frac{1}{T} \\
 -J_y &= L_{13}(-A) \frac{1}{T} \nabla_x \mu + L_{14}(-A) \nabla_x \frac{1}{T} + L_{11}(-A) \frac{1}{T} \nabla_y \mu + L_{12}(-A) \nabla_y \frac{1}{T} \\
 Q_y &= L_{23}(-A) \frac{1}{T} \nabla_x \mu + L_{24}(-A) \nabla_x \frac{1}{T} + L_{21}(-A) \frac{1}{T} \nabla_y \mu + L_{22}(-A) \nabla_y \frac{1}{T}
 \end{aligned} \tag{13-9}$$

Comparing (13-9) with (13-7) we see that the kinetic coefficients connecting x-directed currents with x-directed forces, or y-directed currents with y-directed forces, are even functions of the magnetic field. The coefficients connecting x-directed currents with y-directed forces, or y-directed currents with x-directed forces, are odd functions of the field. But Onsager's Relations, as stated in (9-33), require that the kinetic coefficients have the same symmetry character with respect to the indices as they have with respect to the magnetic field. Therefore the Onsager Relations allow us to write the kinetic equations in the form:

$$\begin{aligned}
-J_x &= L_{11} \frac{1}{T} \nabla_x \mu + L_{12} \nabla_x \frac{1}{T} + L_{13} \frac{1}{T} \nabla_y \mu + L_{14} \nabla_y \frac{1}{T} \\
Q_x &= L_{12} \frac{1}{T} \nabla_x \mu + L_{22} \nabla_x \frac{1}{T} + L_{14} \frac{1}{T} \nabla_y \mu + L_{24} \nabla_y \frac{1}{T} \\
-J_y &= -L_{13} \frac{1}{T} \nabla_x \mu - L_{14} \nabla_x \frac{1}{T} + L_{11} \frac{1}{T} \nabla_y \mu + L_{12} \nabla_y \frac{1}{T} \\
Q_y &= -L_{14} \frac{1}{T} \nabla_x \mu - L_{24} \nabla_x \frac{1}{T} + L_{12} \frac{1}{T} \nabla_y \mu + L_{22} \nabla_y \frac{1}{T}
\end{aligned} \tag{13-10}$$

As in (10-24) and (10-25) the currents may be resolved into the sum of dissipative and non-dissipative parts:

$$\begin{aligned}
\vec{J}_d &= L_{11} \frac{1}{T} \nabla \mu + L_{12} \nabla \frac{1}{T} \\
\vec{Q}_d &= L_{12} \frac{1}{T} \nabla \mu + L_{22} \nabla \frac{1}{T}
\end{aligned} \tag{13-11}$$

and

$$\begin{aligned}
\vec{J}_n &= -L_{13} (\vec{k} \times \frac{1}{T} \nabla \mu) - L_{14} (\vec{k} \times \nabla \frac{1}{T}) \\
\vec{Q}_n &= -L_{14} (\vec{k} \times \frac{1}{T} \nabla \mu) - L_{24} (\vec{k} \times \nabla \frac{1}{T})
\end{aligned} \tag{13-12}$$

where \vec{k} is a unit vector in the z-direction.

The non-dissipative currents are odd functions of the magnetic field, and do not contribute to the production of entropy. The dissipative currents are even functions of the magnetic field, and the dissipation of entropy is

$$\dot{S} = \nabla \frac{1}{T} \cdot \vec{Q}_d - \frac{1}{T} \nabla \mu \cdot \vec{J}_d \tag{13-13}$$

We now apply the kinetic equations (13-10) to an analysis of the various effects in a magnetic field. Several of these effects may be measured in either of two ways, distinguished by Sommerfeld and Frank by the names "isothermal" and "adiabatic". In an isothermal method of

measurement a current (either electric or heat) is allowed to flow in the x-direction and the system is so arranged that there is no temperature gradient in the y-direction. In an adiabatic method of measurement a current is allowed to flow in the x-direction and the system is so arranged that no heat current can flow in the y-direction. We shall consider the isothermal and adiabatic values of the various effects separately.

a - The Isothermal Electrical Conductivity

The isothermal electrical conductivity is defined by

$$\sigma_1 \equiv - \frac{eJ_x}{\nabla_x \left(\frac{\mu}{T} \right)} \quad (13-14)$$

under the conditions

$$\nabla_x T = \nabla_y T = J_y = 0 \quad (13-15)$$

Eliminating $\frac{1}{T} \nabla_y \mu$ from the first and third kinetic equations:

$$-J_x = \left(L_{11} + \frac{L_{13}^2}{L_{11}} \right) \frac{1}{T} \nabla_x \mu$$

whence

$$\sigma_1 = e^2 \frac{L_{11}^2 + L_{13}^2}{T L_{11}} \quad (13-16)$$

b - The Adiabatic Electrical Conductivity

The adiabatic electrical conductivity is defined by

$$\sigma_a \equiv - \frac{eJ_x}{\frac{1}{e} \nabla_x \mu} \quad (13-17)$$

under the conditions

$$\nabla_x T = Q_y = J_y = 0 \quad (13-18)$$

Eliminating $\frac{1}{T} \nabla_y \mu$ and $\nabla_y \frac{1}{T}$ from the first, third and fourth kinetic equations:

$$\sigma_a = \frac{e^2}{TD} \cdot \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix} \quad (13-19)$$

c - The Isothermal Heat Conductivity

The isothermal heat conductivity is defined by

$$\kappa_i \equiv - \frac{Q_x}{\nabla_x T} \quad (13-20)$$

under the conditions

$$J_x = J_y = \nabla_y T = 0 \quad (13-21)$$

Eliminating $\frac{1}{T} \nabla_x \mu$ and $\frac{1}{T} \nabla_y \mu$ from the first, second, and third kinetic

equations:

$$\kappa_i = + \frac{1}{T^2} \begin{vmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{14} \\ -L_{13} & -L_{14} & L_{11} \end{vmatrix} \cdot \begin{vmatrix} L_{11} & L_{13} \\ -L_{13} & L_{11} \end{vmatrix}^{-1} \quad (13-22)$$

d - The Adiabatic Heat Conductivity

The adiabatic heat conductivity is defined by

$$\kappa_a \equiv - \frac{Q_x}{\nabla_x T} \quad (13-23)$$

under the conditions

$$J_x = J_y = Q_y = 0 \quad (13-24)$$

Eliminating $\frac{1}{T} \nabla_x \mu$, $\frac{1}{T} \nabla_y \mu$ and $\nabla_y \frac{1}{T}$ from the kinetic equations:

$$\kappa_a = \frac{1}{T^2} \begin{vmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{12} & L_{22} & L_{14} & L_{24} \\ -L_{13} & -L_{14} & L_{11} & L_{12} \\ -L_{14} & -L_{24} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad \begin{matrix} 102 \\ \\ \\ \end{matrix} \quad (13-25)$$

e - The Isothermal Hall Effect

The isothermal Hall coefficient is defined by

$$(\text{Hall})_1 \equiv - \frac{1}{e} \nabla_y \mu / H_z e J_x \quad (13-26)$$

(where H_z is the magnetic field strength) under the conditions

$$J_y = \nabla_y T = \nabla_x T = 0 \quad (13-27)$$

Eliminating $\frac{1}{T} \nabla_x \mu$ from the first and third kinetic equations:

$$(\text{Hall})_1 = - \frac{T}{e^2 H_z} \frac{L_{13}}{L_{11}^2 + L_{13}^2} \quad (13-28)$$

It should be noted that the adiabatic Hall coefficient, defined as the transverse emf. per unit current and per unit magnetic field, cannot be obtained from our equations. For in the adiabatic effect we do not have $\nabla_y T = 0$, and therefore $\frac{1}{e} \nabla_y \mu \neq \text{emf}$. The adiabatic Hall coefficient is, however, the more commonly measured of the two Hall coefficients.

f - The Isothermal Nernst Effect

The isothermal Nernst coefficient is defined by

$$(\text{Nernst})_1 \equiv - \frac{1}{e} \nabla_y \mu / H_z \nabla_x T \quad (13-29)$$

under the conditions

$$J_x = J_y = \nabla_y T = 0 \quad (13-30)$$

Eliminating $\frac{1}{T} \nabla_x \mu$ from the first and third kinetic equations:

$$(\text{Nernst})_1 = \frac{-1}{eH_z T} \frac{L_{12}L_{13} - L_{11}L_{14}}{L_{11}^2 + L_{13}^2} \quad (13-31)$$

The adiabatic Nernst coefficient, like the adiabatic Hall coefficient, cannot be obtained from our equations.

g - The Ettinghausen Effect

The Ettinghausen coefficient is defined by

$$(\text{Ettinghausen}) \equiv \nabla_y T / H_z e J_x \quad (13-32)$$

under the conditions

$$J_y = Q_y = \nabla_x T = 0 \quad (13-33)$$

Clearly the Ettinghausen effect is an intrinsically adiabatic effect.

Eliminating $\frac{1}{T} \nabla_x \mu$ and $\frac{1}{T} \nabla_y \mu$ from the first, third, and fourth kinetic equations:

$$(\text{Ettinghausen}) = \frac{T^2}{eH_z} (L_{11}L_{14} - L_{12}L_{13}) \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad (13-34)$$

h - The Leduc-Righi Effect

The Leduc-Righi coefficient is defined by the equation

$$(\text{Leduc}) \equiv \nabla_y T / H_z \nabla_x T \quad (13-35)$$

under the conditions

$$J_x = J_y = Q_y = 0 \quad (13-36)$$

Eliminating $\frac{1}{T} \nabla_x \mu$ and $\frac{1}{T} \nabla_y \mu$ from the first, third and fourth kinetic equations:

$$(\text{Leduc}) = \frac{1}{H_z} \cdot \begin{vmatrix} L_{11} & L_{13} & -L_{12} \\ -L_{13} & L_{11} & L_{14} \\ -L_{14} & L_{12} & L_{24} \end{vmatrix} \cdot \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1} \quad (13-37)$$

1 - The Bridgman Relation

By a quasi-thermodynamic argument Bridgman has shown a relation between the isothermal Nernst coefficient and the Ettinghausen coefficient.

We recall

$$(\text{Nernst})_1 = \frac{-1}{eH_z T} \frac{L_{12}L_{13} - L_{11}L_{14}}{L_{11}^2 + L_{13}^2}$$

$$(\text{Ettinghausen}) = \frac{T^2}{eH_z} (L_{11}L_{14} - L_{12}L_{13}) \cdot \begin{vmatrix} L_{11} & L_{13} & L_{14} \\ -L_{13} & L_{11} & L_{12} \\ -L_{14} & L_{12} & L_{22} \end{vmatrix}^{-1}$$

$$\text{and } \kappa_1 = \frac{1}{T^2} \frac{1}{L_{11}^2 + L_{13}^2} \cdot \begin{vmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{14} \\ -L_{13} & -L_{14} & L_{11} \end{vmatrix}$$

Slight manipulation shows that the large determinants appearing in κ_1 and (Ettinghausen) are equal, so that

$$\kappa_1 \text{ (Ettinghausen)} = \frac{1}{eH_z} \frac{L_{11}L_{14} - L_{12}L_{13}}{L_{11}^2 + L_{13}^2}$$

or $\kappa_1 \text{ (Ettinghausen)} = T \text{ (Nernst)}_1$ (13-38)

which is Bridgman's Relation. Another relation, connecting the Hall and Leduc-Righi effects, was at one time proposed by Bridgman (cf. Bridgman I) and is quoted in the literature (cf. Sommerfeld and Frank). However, Bridgman himself later showed the relation to be in error (cf. Bridgman II, p. 151), and our equations support this latter view. In this connection it may be remarked that although we have eight coefficients there are only six independent kinetic coefficients in a magnetic field. There must, therefore, be an additional relation among the coefficients in addition to that given above, (13-38).

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Appointed Teaching Fellow in Physics at Temple University,
1941-1942.

During summer of 1941 attended ESMDT program in Electrical
Engineering at the Moore School of the University of Pennsylvania.

Awarded degree of A.M. in Physics, 1942, Temple University.

Participated in program in Applied Mathematics, Brown University,
during summer of 1942.

Appointed Teaching Fellow in Physics at the Massachusetts
Institute of Technology, 1942-1944.

Employed as Theoretical Physicist by Kellex Corporation,
"Manhattan Project" 1944-1945.

Employed as experimental physicist in Navy Guided Missile
Project, Princeton University, 1945.

Appointed Research Assistant (and later Research Associate)
in the Laboratory for Insulation Research at the Massachusetts
Institute of Technology, 1945-1947. Simultaneously re-entered
Physics Department as a candidate for advanced degree.