THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The Experimental Verification of the Onsager Reciprocal Relations[1]

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I. Introduction

In the last twenty years a thermodynamic theory of irreversible processes (TIP) has been vigorously developed which, unlike its classical forebear, has been able to treat irreversible phenomena in a detailed way. The present macroscopic form of the theory (32, 45, 46, 61, 63, 65, 112, 113, 114, 125, 126, 130, 132) was suggested primarily by the statistical mechanical investigations of Onsager (125, 126). However the necessary concepts, such as entropy production, linear laws, and symmetry of coefficients, are based wholly on experiment and were known long ago. For example, in the case of heat conduction in solids, the entropy production was known at least as early as 1887 (8), the linear laws as early as 1811 (55, 56), and the symmetry of coefficients was suggested in 1851 (148) and first shown experimentally in 1893 (143, 144). If these notions had been generalized and applied to other phenomena, the theory might well have appeared outright in macroscopic form. By historical accident the interrelation of these notions was not recognized until statistical mechanics showed the way. In this review only the macroscopic theory will be considered, leaving aside all statistical considerations.

This theory of irreversible processes has been very successful in treating many sorts of irreversible phenomena. In some cases, such as thermoelectricity and electrical transference in solutions, equations originally derived by admittedly incorrect means have been put on a rational basis. Despite the theory's success, some (5, 6) have considered that it was not adequately verified by experiment. Most of the controversy has been concerned with the validity of the most important consequence of the formalism, the Onsager reciprocal relations. The purpose of this review is to collect the presently available experimental data for a variety of quite different irreversible phenomena and to show that this evidence does indeed verify the Onsager reciprocal relations. Some of the data have been in the literature for years, and part of them were originally obtained to verify less general or incorrect theories. Thermoelectricity, electrokinetics, transference in electrolytic solutions, isothermal diffusion, heat conduction in anisotropic solids, and thermogalvanomagnetic effects will be the irreversible phenomena considered in detail. Chemical reactions and the thermomechanical effects will be discussed briefly.

II. Thermodynamical Preliminaries

To facilitate the thermodynamic description of the various irreversible phenomena to be considered, the assumptions and the general formalism of the theory of irreversible processes will be discussed briefly. This material has been covered more comprehensively in a previous article (116; *cf.* 31, 68).

A. Assumptions

1. Classical thermodynamics

All the concepts of classical thermodynamics are assumed.

2. Division into subsystems

It is assumed that systems undergoing irreversible processes can be divided up into infinitesimal subsystems in which the usual thermodynamical variables such as T, P, V, E, S, etc., have meaning. For example, a heat-conducting rod can be divided up into a large number of thin slices, each of which has a definite temperature. Such an assumption is valid for most processes but would fail in turbulent systems.

3. Local equilibrium

It is assumed that each subsystem can be considered as if it were in local equilibrium, despite the gradients of the thermodynamic variables which give rise to the irreversibility. This assumption permits one to apply all the results of classical thermodynamics to a given subsystem. It will be valid if perturbations from equilibrium are not too large.

B. Sketch of the Formalism

1. The entropy production

By means of the above assumptions, the entropy production can be calculated. This notion is based on the Clausius inequality

$$dS > \sum \frac{\delta q}{T} \qquad \text{(irrev.)} \qquad (1)$$

a theorem of classical thermodynamics (33a). S is the entropy, q is the heat transported across a boundary of the system, T is the temperature of the surroundings at the boundary, δ refers to an inexact differential, and the summation is applied if there are boundaries of the system at different temperatures. Expression 1 can be turned into an equality (the entropy equation) in this manner (63a, 130, 132)

$$dS = \sum \frac{\delta q}{T} + dS_{\text{int}} \qquad (2)$$

where dS_{int} is called the "entropy created internally" during the irreversible process, and by equation 1 is always positive. By means of assumptions 2 and 3, these equations may be applied to any subsystem. The "entropy production" σ is now defined to be the rate of change of S_{int} per unit volume, i.e.,

$$\sigma = \frac{1}{V}\frac{dS_{\text{int}}}{dt} \qquad (3)$$

where t is the time and V is the volume. In any particular case, dS_{int} is calculated from the defining equation 2 as follows: The quantity dS is computed for a

particular subsystem in the usual way by integrating $\delta q/T$ along some *reversible* path between the initial and final states associated with some time interval. Assumption 3 is used in this part of the calculation. Next the quantities $\delta q/T$ at each boundary of the subsystem for the actual irreversible process are calculated and summed. It is often convenient to compute δq by a separate calculation of $dE + \delta w$, where E is the energy and w is the irreversible work done by the system. Substitution into equation 2 gives dS_{int}. (Some simple examples are given in reference 116.)

The quantity $T\sigma$ is known as the "dissipation" and was known to Bertrand (8) in 1887 for the case of heat conduction. Other early workers who calculated σ or $T\sigma$ were Rayleigh (135), Natanson (121), Duhem (39), Jaumann (87, 88), and Lohr (96, 97). More recent calculations are summarized in De Groot's book (63), and many references are given there and by Denbigh (32).

When $T\sigma$ is calculated for any system, it is always found to be of the form

$$T\sigma = \sum J_i X_i \tag{4}$$

or its vector or tensor analogs. The J_i are flows of matter, heat, or electricity, and the X_i are generalized forces such as gradients of chemical potential, temperature, or electrical potential. Take for example, a fluid of k constituents (some of which may be charged), which is situated in a gravitational field and in which gradients of concentration and temperature exist. $T\sigma$ can be written in one-dimensional form for a given subsystem as (117):

$$T\sigma = \left(-\frac{1}{A}\frac{\delta q}{dt}\right)\left[-\frac{1}{T}\frac{dT}{dx}\right] + \sum_k \left(-\frac{1}{A}\frac{dn_k}{dt}\right)\left[-\left(M_k g + e_k\frac{d\phi}{dx} + T\frac{d(\mu_k/T)}{dx}\right)\right] \tag{5}$$

Here A denotes the cross-section, x the length, n_k the number of moles of k, M_k the molecular weight, e_k the electrical charge in faradays, μ_k the chemical potential (the partial molal free energy $\bar{F}_k$), g the acceleration due to gravity, and ϕ the electrical potential. The parentheses are the flows J of heat and matter per unit cross-section, and the square brackets are the generalized forces X. More familiar cases will be considered shortly. It should be remarked again that this sort of calculation depends on assumptions 2 and 3 and would not be possible in systems with turbulence.

2. *The linear laws*

It was noticed experimentally long ago that in simple cases the forces and flows of $T\sigma$ are linearly related to each other. Thus, for example,

(*a*) Pure electrical conduction

$$T\sigma = I\mathcal{E} \tag{6a}$$

$$I = (1/R)\mathcal{E} \qquad \text{Ohm's law (124)} \tag{6b}$$

(*b*) Pure heat conduction

$$T\sigma = J_q\left(-\frac{1}{T}\frac{dT}{dx}\right) \tag{7a}$$

$$J_q = -(K/T)\frac{dT}{dx} \qquad \text{Fourier's law (55, 56)} \tag{7b}$$

where I is the current, $\mathcal{E}$ is the e.m.f., R is the resistance, J_q is the flow of heat, and K/T is the heat conductivity coefficient. Note that equation 6a, the Joule heat, is already familiar as a dissipation energy.

In general if there is more than one irreversible process occurring, it is found experimentally that each flow J_i is not only linearly related to its conjugate force X_i but is also linearly related to all other forces found in the expression for $T\sigma$. If the general linear coefficient is denoted by L_{ij}, the general form for J_i is

$$J_i = \sum_j L_{ij}X_j \tag{8}$$

For example, in thermoelectricity the flow of current is caused by the temperature gradient as well as the usual electric potential gradient. The connection is clear from a microscopic viewpoint, because heat is conducted through metals in part by the transfer of energy from the hotter higher-energy electrons to the cooler lower-energy ones.

3. *The Onsager reciprocal relations*

So far, no ideas have been presented above which were not used extensively before 1900. The only significant addition of this century to the theory of irreversible thermodynamics (63, 125, 126) is the following: *Provided the J_i and X_i are chosen from the expression for $T\sigma$ and are independent, the phenomenological coefficients L_{ij} of the linear laws satisfy the symmetry relation*

$$L_{ij} = L_{ji} \tag{9}$$

for all i and j. In the presence of magnetic fields, equation 9 takes the form

$$L_{ij}(B) = L_{ji}(-B) \tag{10}$$

where B is the magnetic induction.

As noted before, this kind of relation was found for heat conduction in anisotropic solids. However, the first general statement of this principle was given by Onsager (125, 126) in 1931, as a consequence of a statistical mechanical argument. It is known as Onsager's principle, and equation 9 states the Onsager reciprocal relations. The power of this simple relation will be seen in the following sections.

In any theory, certain axioms or principles are assumed. In a purely macroscopic theory, the validity of the axioms and their consequences can be compared directly with experiment. In this way the validity of classical thermodynamics was shown long ago. Similarly, Onsager's principle can be taken as an axiom

supplementary to classical thermodynamics, and its experimental validity investigated. This is a worthwhile task, even in view of the existing statistical mechanical derivations, because the conceptual foundations of equilibrium statistical mechanics alone are the subject of considerable controversy. Even more specialized and controversial hypotheses are required for the derivation of equation 9.

The experimental evidence for the validity of Onsager's reciprocal relations in a wide variety of different irreversible processes will now be exhibited.

III. Thermoelectricity

A. Definitions and description of the effects

Consider a thermocouple consisting of two metals A and B whose junctions in electrical contact are at T and $T + dT$, as shown in figure 1 (63b, 73). As a result

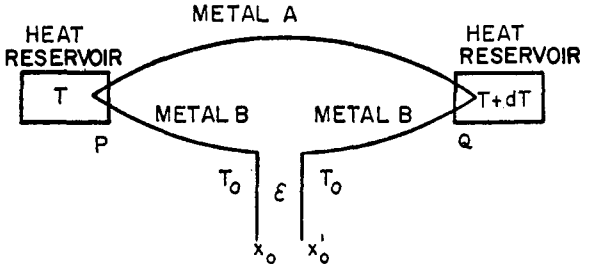

Fig. 1. Schematic diagram of thermocouple. The terminals of a potentiometer (Seebeck effect) or battery (Peltier effect) are at x_0 and x_0'.

of the temperature difference, heat and electricity will flow and potential and thermal gradients will be set up. There are a number of thermoelectric effects depending on the complexity and degree of anisotropy of the system. It is assumed that the above system is isotropic, and only the Seebeck and Peltier effects will be considered.

In the Seebeck effect an e.m.f. $\mathcal{E}$ is measured between the two junctions P and Q when no current is permitted to flow. Thus $\mathcal{E}$ is measured with a potentiometer, whose e.m.f. terminals at x_0 and x_0' are at the same temperature T_0 to avoid thermoelectric e.m.f.'s inside the measuring system. This $\mathcal{E}$ can clearly be written

$$\mathcal{E} = -\int_{x_0}^{x_0'} \left(\frac{d\phi}{dx}\right)_{I=0} dx \tag{11}$$

where ϕ is the electrical potential. Its derivative

$$\frac{d\mathcal{E}}{dT} = -\frac{d\phi}{dx}\frac{dx}{dT} = \frac{-d\phi}{dT} \tag{12}$$

is called the *thermoelectric power*.

In the Peltier effect, the two junctions are kept at the same temperature, but a current is passed through the wires. A quantity of heat J_q will be absorbed at one junction and a quantity $-J_q$ at the other. This quantity of heat is found experimentally to be proportional to the electrical current I; hence the *Peltier heat*, Π, is defined as

$$\Pi = (J_q/I)_{dT=0} \tag{13}$$

B. Derivation of Kelvin's relation

The above system is easily analyzed by the theory of irreversible processes in a very direct way as follows. It can be shown quite easily (63b) that for the thermocouple as a whole

$$T\sigma = J_q\left(-\frac{1}{T}\frac{dT}{dx}\right) \qquad \left(-\frac{d\phi}{dx}\right) \tag{14}$$

Hence the linear relations are

$$J_q = L_{11}\left(-\frac{1}{T}\frac{dT}{dx}\right) + L_{12}\left(-\frac{d\phi}{dx}\right) \tag{15}$$

$$I = L_{21}\left(-\frac{1}{T}\frac{dT}{dx}\right) + L_{22}\left(-\frac{d\phi}{dx}\right) \tag{16}$$

The conditions of the Seebeck experiment are $I = 0$, and thus by equation 16

$$\frac{d\mathcal{E}}{dT} = -\left(\frac{d\phi}{dT}\right)_{I=0} = \frac{L_{21}}{TL_{22}} \tag{17}$$

From the definition of the Peltier heat and equations 15 and 16, one readily obtains:

$$\Pi = (J_q/I)_{dT=0} = \frac{L_{12}}{L_{22}} \tag{18}$$

Thus one has:

$$L_{12}/L_{21} = \Pi/T\frac{d\mathcal{E}}{dT} \tag{19}$$

According to equation 9 $L_{12} = L_{21}$; whence

$$\Pi = T\frac{d\mathcal{E}}{dT} \tag{20}$$

Conversely, if $\Pi = Td\mathcal{E}/dT$, the Onsager reciprocal relation will be verified. Equation 20 is a well-known expression of thermoelectricity, derived by Kelvin in 1854 (152) by an admittedly unjustifiable argument. Until the theory of irreversible processes, many imaginative but incorrect attempts were made to justify it (16a, 47, 48, 153).

More elaborate derivations of Kelvin's relation consider the system to have two components, a fixed metal and moving electrons (21, 36, 37, 122a). Such derivations are helpful in understanding the Thomson heat as well as being valuable in showing the clarification which can result from a wholly macroscopic treatment. The arguments have been extended to anisotropic media by Domenicali (36, 37), whose papers along with Nye's book (122a) are especially recommended.

It can also be shown by means of the theory of irreversible processes that an electrolytic cell whose electrodes are identical except for being at different tem-

peratures and whose solution is of uniform composition behaves in the same way as a metallic thermocouple and will, if the Onsager reciprocal relations are valid, also obey equation 20 (2, 78, 120).

C. EXPERIMENTAL EVIDENCE FOR THE ONSAGER RECIPROCAL RELATION

Not every experimental measurement is suitable for comparison, because it is well known that minor impurities have an enormous effect on the thermoelectric properties of metals. Consequently a test of the validity of the Onsager reciprocal relations for metals will be significant only if $d\mathcal{E}/dT$ and Π are determined on the same specimen. Owing to the difficulty of directly determining Π, not many such measurements exist. In table 1 are the values of Π/T and $d\mathcal{E}/dT$ measured on the same specimen for a number of metallic thermocouples. Table 2 contains the limited data obtained since 1900 for electrolytic thermocouples.

TABLE 1

Test of the Kelvin relation for metallic thermocouples

Couple	Temperature	$\frac{\Pi}{T}$	$\frac{d\mathcal{E}}{dT}$*	$\frac{\Pi}{T\,d\mathcal{E}/dT} = \frac{L_{12}}{L_{21}}$	Reference
	°C.				
Cu–Ag	0	−1.8	−2.1	0.86	(82)
	18	0.1	0.2	0.5	(27)
Cu–Al	15.8	2.4	3.1	0.77	(27)
Cu–Ni	0	18.6	20.0	0.930	(82)
	14	20.2	20.7	0.976	(7)
	22	20.5	22.3	0.919	(27)
Cu–Pt	0	3.66	3.67	0.997	(10)
Cu–Fe	0	−10.16	−10.15	1.000	(10)
	19	−9.9	−12.9	0.77	(60)
	0	−13.22	−13.24	0.998	(4)
Cu–German silver	0	25.25	25.22	1.001	(10)
Cu–Nickeline	0	18.90	18.88	1.001	(10)
Cu–(70% Sn, 30% Pt)	0	2.30	2.32	0.991	(10)
Cu–(70% Pd, 30% Pt)	0	1.06	1.01	1.05	(10)
Cu–Hg	13.9	61.9	61.9	1.00	(150)
	56.2	73.6	73.5	1.00	(150)
	77.7	79.0	79.4	0.995	(150)
	99.7	84.9	85.4	0.994	(150)
	132.2	92.8	94.6	0.980	(150)
	184.4	107.6	108.0	0.996	(150)
Cu–$Bi_\perp$	20	−47	−47	1.00	(12)
Cu–$Bi_\parallel$	20	−71	−66	1.08	(12)
Cu–(Bi 45° from hexagonal axis)	20	−82	−81	1.01	(12)
Cu–Bi	20	−65.9	−67.2	0.98	(28)
Cu–Bi (3.75% Sn)	20	37.0	35.4	1.04	(28)
Cu–Bi (6.36% Sn)	20	39.8	42.7	0.93	(28)
Cu–Bi (9.93% Sn)	20	35.6	38.0	0.94	(28)
Cu–Constantan	15	35.3	35.7	0.989	(7)
	20	37.7	38.9	1.03	(159)
	30	40.5	41.8	1.03	(159)
	40	43.2	44.6	1.03	(159)
Fe–Ni	16	33.1	31.2	1.06	(7)
Fe–Hg	18.4	16.72	16.66	1.004	(128)
	56.5	16.17	16.14	1.002	(128)
	99.6	15.57	15.42	1.010	(128)
	131.6	14.89	14.81	1.005	(128)
	182.3	13.88	13.74	1.011	(128)
Fe–Al	0	11.0	11.5	0.956	(4)
Fe–German silver	0	19.97	20.0	0.998	(4)
Cd–Ni	17	22.1	22.6	0.978	(7)
Cd–Pb	0	3.03	3.02	1.00	(4)
Zn–Ni	17	22.1	22.0	1.00	(7)
Zn–Sn	0	2.65	2.56	1.04	(4)
Zn–Bi	0	25.4	25.1	1.01	(4)
Bi_0–Bi_{90}	27	46.0	48.3	0.95	(50)
Bi_{45}–Bi_{90}	27	33.0	27.7	1.15	(50)
Bi–Pb	0	−17.5	−17.2	1.02	(4)

* All values are in microvolts per degree.

TABLE 2

Test of the Kelvin relation for electrolytic thermocouples

Couple	Electrolyte Concentration	Temperature	Π	$zF\,T\,d\mathcal{E}/dT$	$\frac{\Pi}{zF\,T\,d\mathcal{E}/dT}$
	moles/liter	°C.	*kcal./mole*	*kcal./mole*	
Cu–$CuSO_4$	2	25	10.8 (17)*	10.9 (19)*	0.99
Cu–$CuSO_4$	1	~25	8.9 (14)	8.9 (14)	1.00
Cu–H_2SO_4	0.01				
Hg–Hg_2Cl_2	Satd.	25	7.1 (94)	8.2 (92)	0.87
Hg–KCl	1				
Ag–$AgNO_3$	0.01	25	−4.65 (93)	−4.47 (93)	1.03
	0.1	25	−2.93 (93)	−2.89 (93)	1.02
	0.316	25	−2.30 (93)	−2.13 (93)	1.08
	1.0	25	−1.82 (93)	−1.38 (93)	1.32

* References are given in parentheses.

The ratio L_{12}/L_{21} is remarkably close to unity in all but a few cases, leaving no doubt that the Onsager reciprocal relation is verified within the error of the experiments.

IV. ELECTROKINETICS

A. DEFINITIONS AND DESCRIPTION OF THE EFFECTS

Some of the various electrokinetic quantities (59, 104a) will now be taken up. Consider a fluid system which may have several components (some of which may be charged), and suppose this system divided into two reservoirs separated by a porous diaphragm. The diaphragm may be a single capillary, a porous frit, or even pressed fibers such as compressed glass wool. Into each reservoir dips an electrode as shown in the schematic diagram of figure 2.

If a fixed potential difference $\mathcal{E}$ is impressed across the electrodes, then it is found that as a consequence of the current flow I, a fluid flow J through the diaphragm D results until finally a steady state is reached. At this point the pressure difference $\Delta P = P_2 - P_1$ just balances the impressed $\mathcal{E}$, and the flow J becomes zero. The observed ΔP depends on both the fluid and the nature of the diaphragm but is proportional to $\mathcal{E}$. The forced flow of fluid through a diaphragm by an

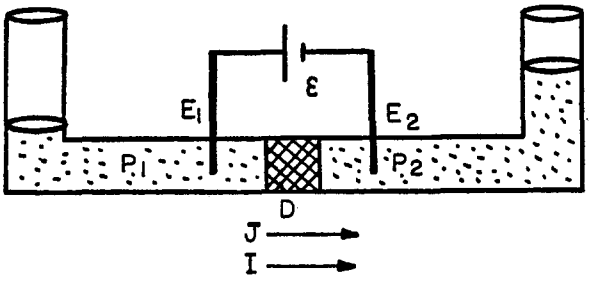

FIG. 2. Schematic diagram of apparatus to measure electroosmotic pressure.

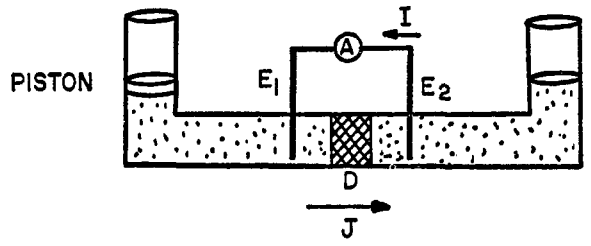

FIG. 3. Schematic diagram of apparatus to measure streaming current.

impressed e.m.f. is called electroösmosis. Thus for a given system and diaphragm, the *electroösmotic pressure* (EOP) can be defined as

$$\text{EOP} = (\Delta P/\mathcal{E})_{J=0} \tag{21}$$

Now consider the converse experiment with the same fluid and diaphragm in which the electrodes are short circuited (i.e., $\mathcal{E} = 0$) and the fluid forced through the diaphragm by a piston as shown in figure 3. If an ammeter A is placed between the electrodes, a current I is observed which is proportional to J but depends on the fluid and the diaphragm. A quantity called the *streaming current* (SC) can be defined as

$$\text{SC} = (I/J)_{\mathcal{E}=0} \tag{22}$$

There are various other combinations of experimental conditions which lead to other defined quantities. Thus if the fluid is forced through the diaphragm with a pressure difference ΔP, and the $\mathcal{E}$ resulting is measured with a potentiometer ($I = 0$), then the *streaming potential* (SP) can be defined as

$$\text{SP} = (\mathcal{E}/\Delta P)_{I=0} \tag{23}$$

Similarly, when an $\mathcal{E}$ forces the fluid through the diaphragm along a horizontal tube so that $\Delta P = 0$, both J and I can be measured, giving rise to the quantities *electroösmosis* (EO),

$$\text{EO} = (J/I)_{\Delta P=0} \tag{24}$$

and *2nd electroösmosis*

$$\text{2nd EO} = (J/\mathcal{E})_{\Delta P=0} \tag{25}$$

All of these quantities, as well as the resistance R, have been measured in the experiments that will be used to test the Onsager reciprocal relations.

B. DERIVATION OF SAXÈN'S AND RELATED EQUATIONS

The general situation may be analyzed by the theory of irreversible processes (63c, 100, 101, 108, 109, 116, 129, 132a). It has been shown that the entropy production for this type of system is

$$T\sigma = J\Delta P + I\mathcal{E} \tag{26}$$

so that the linear laws are

$$J = L_{11}\Delta P + L_{12}\mathcal{E} \tag{27a}$$

$$I = L_{21}\Delta P + L_{22}\mathcal{E} \tag{27b}$$

It is easily seen that

$$\text{EOP} = (\Delta P/\mathcal{E})_{J=0} = -L_{12}/L_{11} \tag{28}$$

$$\text{SC} = (I/J)_{\mathcal{E}=0} = L_{21}/L_{11} \tag{29}$$

$$\text{SP} = (\mathcal{E}/\Delta P)_{I=0} = -L_{21}/L_{22} \tag{30}$$

$$\text{EO} = (J/I)_{\Delta P=0} = L_{12}/L_{22} \tag{31}$$

$$\text{2nd EO} = (J/\mathcal{E})_{\Delta P=0} = L_{12} \tag{32}$$

$$R = (\mathcal{E}/I)_{\Delta P=0} = 1/L_{22} \tag{33}$$

It is clear that the assumption $L_{12} = L_{21}$ entails various relations among the experimental quantities; e.g.,

$$\text{EOP} = -\text{SC} \tag{34}$$

$$-\text{EO} = \text{SP} \tag{35}$$

$$-(\text{2nd EO})\text{R} = \text{SP} \tag{36}$$

Conversely, the validity of these relations entails $L_{12} = L_{21}$.

The first of these, equation 34, is known as Saxèn's relation and was originally derived using microscopic models of the details of the electrokinetic process (139). The analysis assuming the Onsager reciprocal relations shows that this result, and the others as well, should be valid independently of any models.

C. DATA AND VERIFICATION OF THE ONSAGER RECIPROCAL RELATION

It should be remarked that electrokinetic experiments have the same sort of difficulty as thermoelectric ones. Two ostensibly identical diaphragms may behave quite differently. Results even on the same diaphragm may change with time and are very sensitive to impurities, especially in dilute solutions. The data collected below have been determined on systems which used the *same diaphragm* for the different kinds of electrokinetic measurements.

Table 3 (139) contains the experimental evidence for Saxèn's relation, and table 4 (38) contains that for equation 35. These latter results are stated to have significant experimental error.

TABLE 3

Test of Saxèn's relation (139)

Clay Plugs; Aqueous Solution	$\frac{-1^*}{\text{SC}}$	$\frac{1^*}{\text{EOP}}$	$\frac{-\text{EOP}}{\text{SC}} = \frac{L_{12}}{L_{21}}$
½% $ZnSO_4$	0.356	0.352	1.01
¾% $ZnSO_4$	0.386	0.388	0.99
	0.377	0.377	1.00
	0.381	0.379	1.01
1% $ZnSO_4$	0.350	0.338	1.04
	0.342	0.350	0.98
1% $CuSO_4$	0.392	0.380	1.03
	0.385	0.389	0.99
	0.378	0.387	0.95
2% $CuSO_4$	0.233	0.237	0.98
½% $CdSO_4$	0.633	0.609	1.04
1% $CdSO_4$	0.532	0.567	0.94
	0.116	0.115	1.01

* 1/SC and 1/EOP are given in $cm.^{5/2}/g.^{1/2}$.

TABLE 4

Test of equation 35 (38)

Glass Slit: Concentration of Aqueous Solution	KCl			$BaCl_2$			$AlCl_3$		
	$-EO \times 10^{10}$	$SP \times 10^{10}$	$\frac{-EO}{SP}$	$-EO \times 10^{10}$	$SP \times 10^{10}$	$\frac{-EO}{SP}$	$-EO \times 10^{10}$	$SP \times 10^{10}$	$\frac{-EO}{SP}$
equiv./liter	*cc./sec e.s.u.*	*e.s.u. cm.²/dyne*		*cc./sec. e.s.u.*	*e.s.u. cm.²/dyne*		*cc./sec. e.s.u.*	*e.s.u. cm.²/dyne*	
10^{-4}	132	95.0	1.4	77.9	62.2	1.25	70.9	80	0.88
5×10^{-4}	11.2	18.5	0.61	12.4	11.8	1.05	15.7	16.6	0.94
10^{-3}	9.9	8.0	1.23	4.8	5.3	0.91	7.0	8.1	0.87

T ≅ 23°C.

Much of the data for verifying equation 36 have been reported in terms of the zeta potential ζ, a concept based on the microscopic models. The ζ potential is defined in terms of 2nd electroösmosis by

$$-\zeta_{EO} = \frac{4\eta l(J/\mathcal{E})_{\Delta P=0}}{Dr^2} \tag{37}$$

and in terms of streaming potential and R by

$$\zeta_{SP} = \frac{4\eta l(\mathcal{E}/\Delta P)_{I=0}}{RDr^2} \tag{38}$$

where η is the viscosity of the fluid and D its dielectric constant. The quantities r and l are the radius and length of a diaphragm consisting of a single capillary. If the diaphragm is a porous frit, l/r^2 is replaced by the equivalent quantity πK referring to the network of capillaries making up the frit, where K is the effective cell constant for conductivity and is the same for both ζ_{EO} and ζ_{SP}. If equation 32 is substituted into equation 37 and if equations 30 and 33 are substituted into equation 38, one obtains:

$$\zeta_{EO} = -L_{12}[4\eta l/Dr^2] \tag{39}$$

$$\zeta_{SP} = -\frac{L_{21}}{L_{22}}\left(\frac{1}{R}\right)[4\eta l/Dr^2] = -L_{21}[4\eta l/Dr^2] \tag{40}$$

Thus

$$\zeta_{EO}/\zeta_{SP} = L_{12}/L_{21} \tag{41}$$

The evidence that $\zeta_{EO}/\zeta_{SP} = 1$ is given in tables 5 (18), 6 (136), and 7 (158). The data in table 5 actually were not obtained from the same diaphragm but from a protein-covered capillary (SP) and an electrophoresis cell covered with the same protein. The larger deviations from 1.00 in table 5 compared to those in tables 6 and 7 may be due to this circumstance.

In table 8 are calculated values of L_{12} and L_{21} for quartz–acetone, based on 2nd electroösmosis, streaming potential, and R (102).

Also included are L_{ij} determined using sinusoidally varying voltage and pressure (29). This kind of experiment gives values of L_{ij} which are frequency dependent. However, the values approach a constant value at sufficiently low frequency. In the table only these low-frequency values are included. It is interesting to note

TABLE 5

Test of equation 36 (18)

Protein-covered Pyrex; Aqueous Solution	HCl	$\zeta_{EO}/\zeta_{SP} = L_{12}/L_{21}$
	moles/liter	
0.202% egg albumin	3.5×10^{-4}	0.96
0.174% gelatin	5×10^{-4}	0.95
0.166% gelatin	6.3×10^{-4}	0.79
0.166% gelatin	7.0×10^{-4}	1.19
0.180% gelatin	7.5×10^{-4}	1.45
0.175% gelatin	7.5×10^{-4}	0.82
0.226% gelatin	8.0×10^{-4}	1.07
0.207% gelatin	6.5×10^{-4}	1.14
0.219% gelatin	5×10^{-4}	1.03

T = 25°C.

that $L_{12}/L_{21} = 1$ within the experimental error even at higher frequencies. Above 200 cycles per second phase differences cause difficulty.

Considering the well-known difficulty of carrying out these experiments, it is clear that $L_{12} = L_{21}$ within experimental uncertainties.

There are also some recent electroösmosis and streaming current data of Rutgers and de Smet (137) for isoamylammonium picrate in organic solvents, but they found that the EO was dependent on $\mathcal{E}$, which implies that the linear laws (equation 27) are not adequate for this system. However at low values of $\mathcal{E}$, the linear approximation will become better, and if ζ_{EO} at the lowest value of $\mathcal{E}$ is compared with ζ_{SC} at concentrations of 1 μequiv./l. or larger, the ratio is close to 1.

V. Transference in Electrolytic Solutions

The relation between certain electrochemical effects in an isothermal system consisting of a single binary electrolyte in a neutral solvent will now be considered: namely, Hittorf transference and electrochemical cells with transference.[2]

[2] This simple case has been chosen for review because it is the only one for which the cell e.m.f. is independent of the way in which the liquid junction is formed. Systems with more than one electrolyte can be analyzed in the same way as this one (117), but the e.m.f. depends on the concentration distribution in the junction, and thus in general will be a function of time. To the author's knowledge, no e.m.f. experiments have ever been carried out on these more complex systems to determine transference numbers.

A. THE TIP EQUATIONS

Suppose the electrolyte CA ionizes into cations C and anions A as follows:

$$CA = r_1C^{z_1} + r_2A^{z_2} \quad (42)$$

where r_1 and r_2 are the ionization stoichiometric coefficients for cations and anions and z_1 and z_2 are the charges on the ions with due regard to sign. Let μ_{12} represent the chemical potential of the electrolyte as a whole. Then by definition

$$\mu_{12} = r_1\mu_1 + r_2\mu_2 \quad (43)$$

where μ_1 and μ_2 are the chemical parts of the chemical potential per mole of the ions; moreover,

$$r_1z_1 + r_2z_2 = 0 \quad (44)$$

TABLE 6

Test of equation 36 (136)

Jena 16 III Capillary; Concentration in μ Equivalents per Liter of Aqueous Solution	KCl; Capillary A, r = 0.0243 cm.			KCl; Capillary B, r = 0.0152 cm.			KCl; Capillary C, r = 0.0109 cm.			KCl; Capillary D, r = 0.00516 cm.		
	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$
	mv.	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*	
0	149	159	0.94	152	160	0.95	153	168	0.91	156	155	0.99
1	147	165	0.89	144	155	0.93	147	153	0.96	149	152	0.98
2	146	158	0.92	139	150	0.93	143	151	0.95	145	147	0.99
5	144	155	0.93	139	144	0.97	139	148	0.94	142	145	0.98
10	141	148	0.95	132	141	0.94	136	144	0.94	136	141	0.96
20	139	145	0.89	130	136	0.96	136	138	0.99	135	137	0.99
50	133	138	0.96	124	129	0.96	127	133	0.96	123	127	0.97
100	122	129	0.95	116	123	0.94	119	126	0.94	116	119	0.97
200	118	130	0.91	110	113	0.97	113	120	0.94	107	107	1.00
	HCl; Capillary D			KOH; Capillary D			$CaCl_2$; Capillary D			$Al(NO_3)_3$; Capillary D		
	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$
	mv.	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*	
0												
1	132	135	0.98	153	156	0.98	122	123	0.99	130	132	0.98
2	122	124	0.98	149	156	0.96	115	117	0.98	120	121	0.99
5	100	104	0.96	153	157	0.97	107	108	0.99	60	64	0.94
10	73	77	0.95	154	165	0.93	99	101	0.98			
20	61	61	1.00	153	162	0.94	91	92	0.99			
50				151	153	0.99	81	82	0.99	−42	−38	1.11
100				146	152	0.96	75	76	0.99	−44	−46	0.96
200				139	139	1.00	69	69	1.00			

Values for hydrochloric acid, potassium hydroxide, calcium chloride, and aluminum nitrate were read from the graphs given in reference 136. T = 22.5°C.

TABLE 7

Test of equation 36 (158)

Concentration in μ Equivalents per Liter of Aqueous Solution	KNO_3; Pyrex Capillary			KOH; Pyrex Capillary			$Ba(NO_3)_2$; Pyrex Capillary			$Ca(NO_3)_2$; Pyrex Capillary			KNO_3; Pyrex Powder		
	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$	ζ_{EO}	ζ_{SP}	$\frac{\zeta_{EO}}{\zeta_{SP}}$
	mv.	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*		*mv.*	*mv.*	
0							139.8	138	1.01						
2							111	115	1.04	68.0	68.5	0.99			
5	145	133	0.92	150	151	0.99	101	101.5	1.00	59.0	56.5	0.99	76	80	0.95
10	141.9	130	0.92	155.8	154	0.99	93.5	94	0.99	52.3	52.1	1.00	81	84	0.97
20	136.8	125.5	0.92	153	154	0.99	85.5	86.3	0.99	45.7	45.8	1.00	86	89	0.97
50				147.9	147	1.01	75.3	75.2	1.00	37.5	38.1	0.98	92.5	95	0.97
100	119.2	119	1.00	142.2	142	1.00	67.7	67.5	1.00	31.6	31.7	1.00	95	97.5	0.97
200	111.8	110.5	1.01	136.0	136.5	1.00	60.5	60.2	1.00	25.5	25.5	1.00	97	99	0.98
300													98	100	0.98
Average T	18°C.	16°C.		19°C.	19°C.		19°C.	20°C.		19°C.	19°C.		23°C.	19°C.	

Values of ζ_{SP} for barium nitrate (capillary), lanthanum nitrate (capillary), and potassium nitrate (powder) were from a graph based on data on Wijga's tables IV, V, and XXV, respectively.

Values of ζ_{EO} for potassium nitrate (powder) were obtained from a graph of data in tables XIX and XX. Note that the greatest deviations in the values of ζ are for systems whose temperatures for the measurement of EO and SP differed the most.

TABLE 8

Test of equation 9

System	L_{12}	L_{21}	$\frac{L_{12}}{L_{21}}$	Pressure Frequency	Reference
	c.g.s.-e.s.u.	*c.g.s.-e.s.u.*		*cycles/sec.*	
Quartz powder plug–acetone..	0.028	0.029 ± 0.002	0.96 ± 0.08	0	(102)
Glass frit–water:					
A.....	0.066	0.074	0.89	20	(29)
B.....	0.060	0.056	1.07	20	(29)
C.....	0.053	0.058	0.91	20	(29)
D.....	0.072	0.073	0.99	20	(29)
Glass capillary–water.....	0.00050	0.00045	1.11	40	(29)

Cooke's L_{ij} and Lorenz's c_{ij} correspond to our L_{ji}.

Lorenz's experiments were at 30°C.

The maximum estimated error in each of Cooke's L_{ij} is 6 per cent, or 9 per cent overall.

For such a system (63d),

$$T\sigma = J_1X_1 + J_2X_2 + J_3X_3 \tag{45}$$

$$X_i = -\left[\frac{d\mu_i}{dx} + z_i\mathfrak{F}\frac{d\phi}{dx}\right] \tag{46}$$

where the subscript 3 refers to the solvent ($z_3 = 0$), ϕ is the electrical potential, and $\mathfrak{F}$ is the faraday. It was mentioned earlier that for the Onsager reciprocal relations to be valid, the J_i or X_i or both must be independent. This is not the case here, since the Gibbs–Duhem equation relates the chemical potentials. Thus

$$n_{12}d\mu_{12} + n_3d\mu_3 = 0 = n_{12}(r_1d\mu_1 + r_2d\mu_2) + n_3d\mu_3$$
$$= n_1d\mu_1 + n_2d\mu_2 + n_3d\mu_3 \tag{47}$$

where n_i is the number of moles. However, by equations 46 and 44, this result is equivalent to

$$n_1X_1 + n_2X_2 + n_3X_3 = 0 \tag{48}$$

Therefore, by eliminating X_3, equation 45 is obtained in the independent form:

$$T\sigma = \left(J_1 - \frac{n_1J_3}{n_3}\right)X_1 + \left(J_2 - \frac{n_2J_3}{n_3}\right)X_2 \tag{49}$$
$$= J_1'X_1 + J_2'X_2$$

The flows J_i' can be looked on as motion relative to the solvent, whereas J_i are flows relative to the apparatus. The linear laws written in terms of J' and X_i are now suitable for testing the Onsager reciprocal relations. They are

$$J_1' = L_{11}X_1 + L_{12}X_2 \tag{50}$$

$$J_2' = L_{21}X_1 + L_{22}X_2 \tag{51}$$

B. HITTORF TRANSFERENCE (104b)

Suppose a current I is passed through the system, with the solution at uniform composition throughout. The *Hittorf transference number*, t_i^h, can be defined as the fraction of the current carried by the i^{th} ion relative to the solvent.[3]

The current (in faradays) is

$$I = z_1J_1' + z_2J_2' = z_1J_1 + z_2J_2 \tag{52}$$

hence

$$t_i^h \equiv \frac{z_iJ_i'}{z_1J_1' + z_2J_2'} \quad \text{(uniform composition)} \tag{53}$$

At uniform composition, however,

$$\frac{d\mu_i}{dx} = \frac{d\mu_i}{dm}\frac{dm}{dx} = 0 \tag{54}$$

where m is the molality; hence

$$X_i = -z_i\mathfrak{F}\frac{d\phi}{dx} \quad \text{(uniform composition)} \tag{55}$$

Thus by equations 50, 51, and 55,

$$t_1^h = \frac{z_1(z_1L_{11} + z_2L_{12})}{z_1^2L_{11} + z_1z_2(L_{12} + L_{21}) + z_2^2L_{22}} \tag{56}$$

and similarly for t_2^h.

C. ELECTROCHEMICAL CELLS WITH TRANSFERENCE (32a, 117, 157)

Now consider an electrochemical cell which has two identical electrodes and a single electrolyte but which may have a varying composition, e.g.,

$$\text{Pb} \mid \text{PbCl}_2(m_1) \vdots \text{PbCl}_2(m_2) \mid \text{Pb}$$

where m_i is the molality. In such a system diffusion will occur, and owing to the different mobilities of the ions a charge separation will be induced. After a very short time, much less than a microsecond, however, the powerful coulombic effects speed up the slow ions and slow down the fast ones so that no electric current flows through the solution. Thus

$$I = 0 = z_1J_1' + z_2J_2' \tag{57}$$

a relation expressing the condition of electroneutrality.

From this expression, the liquid-junction (diffusion) potential is calculated by substituting equations 50 and 51 in equation 57, applying equation 46, and finally solving for $\mathfrak{F}d\phi$. The result is

$$-\mathfrak{F}d\phi = \frac{(z_1L_{11} + z_2L_{21})d\mu_1 + (z_1L_{12} + z_2L_{22})d\mu_2}{z_1^2L_{11} + z_1z_2(L_{12} + L_{21}) + z_2^2L_{22}} \tag{58}$$

Now define the *cell* or *e.m.f. transference number* t_1^e of ion 1 to be

$$\frac{t_1^e}{z_1} \equiv \frac{z_1L_{11} + z_2L_{21}}{z_1^2L_{11} + z_1z_2(L_{12} + L_{21}) + z_2^2L_{22}} \tag{59}$$

[3] A rigorous general definition of the Hittorf transference number valid for nonelectrolytes as well as ions and based on the actual experiment is given in reference 117. The analysis in detail, using the flows J_i, yields (equation 17 (117)) our equation 53 based on the definitions above.

and analogously for ion 2. Then the diffusion potential becomes

$$-\mathfrak{F}d\phi = \frac{t_1^c}{z_1} d\mu_1 + \frac{t_2^c}{z_2} d\mu_2 \quad (60)$$

Note that these transference numbers need not be the same as the corresponding Hittorf number; they will be identical only if $L_{12} = L_{21}$.

It should be emphasized that the classical derivation of the diffusion potential, due essentially to Helmholtz (75), is *not* correct, because this system is *irreversible* owing to diffusion. Classical methods can be used only if the states are in equilibrium.

Since the quantities ϕ, μ_1, and μ_2 are not experimentally accessible, it is necessary to consider the whole cell including the electrodes. Of the two ways to include the electrodes, the most familiar is the one given in most chemical thermodynamics or electrochemistry texts and is based on passing a faraday through the cell. A better way (33b, 64, 138) is based on the equilibrium between electrons, electrode, and solution which exists during a potentiometric measurement. The results are of course the same, and for a concentration cell whose electrodes are reversible to the anion are

$$\mathfrak{F}\mathcal{E} = -\int_\alpha^\beta \frac{t_1^c}{r_1 z_1} d\mu_{12} \quad (61)$$

where $\mathcal{E}$ is the potential difference measured at the potentiometer terminals, and α and β represent the anode and cathode, respectively. For electrodes reversible to the cation, replace the subscript 1 in t_1^c, r_1, and z_1 by subscript 2.

Since the chemical potential in terms of the activity a is

$$\mu_{12} = \mu_{12}^0 + \hat{R}T \ln a_{12} \quad (62)$$

where $\hat{R}$ is the gas constant, equation 61 can be written:

$$\frac{\mathfrak{F}\mathcal{E}}{\hat{R}T} = -\int_\alpha^\beta \frac{t_1^c}{r_1 z_1} d \ln a_{12} \quad (63)$$

Thus if a series of measurements of $\mathcal{E}$ is done at various concentrations and if the activity a_{12} is already known by other means, t_1^c is obtained from the experimental quantities using the derivative of equation 63; namely,

$$t_1^c = -\frac{r_1 z_1 \mathfrak{F}}{\hat{R}T} \cdot \frac{d\mathcal{E}}{d \ln a_{12}} \quad (64)$$

Sometimes $\ln a_{12}$ is obtained from e.m.f. measurements on cells *without* transference, for which the differential e.m.f. $d\mathcal{E}^*$ is

$$d\mathcal{E}^* = \frac{\hat{R}T}{r_1 z_1 \mathfrak{F}} d \ln a_{12} \quad (65)$$

Consequently t_1^c is often obtained from the equation

$$t_1^c = \frac{d\mathcal{E}}{d\mathcal{E}^*} \quad (66)$$

D. THE ONSAGER RECIPROCAL RELATION AND ITS EXPERIMENTAL VERIFICATION

If, as is ordinarily assumed, the Hittorf and cell transference numbers are the same, then from equations 56 and 59

$$\frac{t_1^h}{z_1} = \frac{z_1 L_{11} + z_2 L_{12}}{\sum_{i,j} z_i z_j L_{ij}} = \frac{z_1 L_{11} + z_2 L_{21}}{\sum_{i,j} z_i z_j L_{ij}} = \frac{t_1^c}{z_1} \quad (67)$$

Clearly the equality of t_1^h and t_1^c entails the Onsager reciprocal relation

$$L_{12} = L_{21} \quad (68)$$

for electrochemical systems with transference.

In table 9 are collected the t_1^c and t_1^h for a number of salts which were investigated at a number of concentrations. In table 10 are some for which a fewer number of comparisons were possible. In cases where no Hittorf measurements are available, the equivalent moving boundary results are given. It should be noted that the measurements of t_1^c are more difficult, since they involve the differentiation of two sets of experimental data, magnifying the errors of each set.

In table 11 are some less accurate transference data, denoted by t_1^g, determined from gravitational and centrifugal cells. The equations were not derived above, but the argument is essentially the same as for the case of the concentration cell (117). The definition of t_1^g is *exactly* the same as that of t_1^c involving exactly the same numerical values of L_{ij} (apart from a negligible pressure dependency). The data on chlorides were obtained with gravitational cells for which the $\mathcal{E}$ is only a few microvolts per meter. Considering the difficulty of such measurements, the agreement is remarkably good. The centrifugal cell measurements on the iodides were done with modern techniques, but potassium iodide is the only case where a Hittorf or moving boundary measurement exists at the same T and concentration.

The references are preceded by E, H, M, and G for cell, Hittorf, moving boundary, and gravity-centrifugal measurements, respectively. If the temperature of measurement is other than 25°C., it is noted in °C. in parentheses after the value of t_1. The quantities c and m are concentrations in moles per liter and moles per kilogram of solvent, respectively.

The agreement between the two types of transference numbers is very good and within the errors of experiment. However, by equation 67 if $z_1 z_2 L_{12}$ is small compared to $\Sigma_j z_i z_j L_{ij}$, a small error in $t_1^c - t_1^h$ will result in a large per cent error in $L_{12} - L_{21}$. Electrolyte theory (127) does in fact predict that L_{12} will be relatively small, being zero at infinite dilution and increasing as the concentration (and the ionic interaction) increases. Some (unpublished) rough calculations from experimental data indicate that the per cent error in $(L_{12} - L_{21})/L_{12}$ is very roughly $10\Lambda(t_1^h - t_1^c)/m^{1/3}$ for strong

TABLE 9

Test of equation 67 (concentration cells)

Salt		Concentration in c or m								Reference
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	
HCl*	t_1^c	0.831	0.832	0.834	0.836	0.838		0.843	0.845	E (71)
18°C.	t_1^h	0.832	0.833	0.833	0.834	0.835		0.840	0.844	H (81)
HCl	t_1^c	0.824	0.825	0.827	0.830	0.830				E (71)
25°C.	t_1^h	0.824	0.825	0.827	0.829	0.831				M (98)
LiCl	t_1^c	0.335	0.333	0.331	0.326	0.320	0.313	0.307	0.281	E (89)
25°C.	t_1^h	0.330	0.329	0.327	0.323	0.319	0.312	0.301	0.287	H (89)
$BaCl_2$	t_1^c	0.443	0.440	0.436	0.427	0.418	0.405	0.381	0.353	E (90)
25°C.	t_1^h	0.440	0.438	0.433	0.425	0.416	0.403	0.379	0.353	H (90)
KI	t_1^c		0.497	0.497	0.495	0.494		0.488		E (58)
25°C.	t_1^h		0.488	0.488	0.488	0.488		0.489		M (99)
H_2SO_4†	t_1^c				0.825	0.825	0.824	0.820	0.813	E (70)
20°C.	t_1^h				0.822	0.822	0.820	0.816	0.812	H (81)
$CdSO_4$‡	t_1^c		0.397	0.390	0.375	0.358	0.338	0.291	0.244	E (15)
	t_1^h (18°)		0.385	0.379	0.366	0.352	0.330	0.293	0.254	H (84)
$CdBr_2$‡	t_1^c		0.434	0.434	0.425	0.408	0.371			E (103)
	t_1^h (18°)		0.434	0.434	0.431	0.411	0.370			H (83)

* Agreement also at 10°, 30°, and 50°C. † t_1^c at 20°C. from interpolation of Hamer's values (70) at other temperatures.
‡ Some values determined by interpolation from graphs of reported data.

TABLE 10

Test of equation 67 (concentration cells)

Salt	t_1^c	t_1^h	c	Reference
ZnI_2*	0.330	0.325	0.325	E (149)
	0.270	0.273	1.277	H (76)
	−0.150	−0.157	4.73	
$ZnCl_2$	−0.088	−0.08	2.64	E (72)
	−0.260	−0.241	4.035	H (77)

* Values of t_1^c obtained from interpolation from graph of data of Stokes and Levien (149).

1-1 electrolytes, where Λ is the equivalent conductance, and is ⅓ smaller for 2-1 electrolytes. Thus for 1-1 salts, a 0.001 difference in $t_1^h - t_1^c$ is approximately an error of 10, 4, 2, and 1 per cent at 0.001, 0.01, 0.1, and 1.0 molal, respectively, and is four times as large for acids. On this rough basis, it may be concluded that the Onsager reciprocal relations are verified to within about 10 per cent for hydrochloric acid (25°C.), lithium chloride, barium chloride, and cadmium bromide (table 9), zinc chloride and zinc iodide (table 10), and potassium iodide (table 11).

Thus an adequate verification for the Onsager reciprocal relations has been found for most of the cases in tables 9 and 10 (and for potassium iodide in table 11). In the remaining ones, the experimental errors are too large to give a satisfactory test. Moreover, for a test of the Onsager reciprocal relation to be significant to 1 per cent in dilute solutions, both types of transference numbers must be known to 1 to 5 parts in 10,000. As yet, this accuracy has not been achieved in any e.m.f. measurements.

VI. Isothermal Diffusion

Diffusion is a phenomenon well described by the theory of irreversible processes. Owing to the Gibbs-Duhem equation and the experimental condition of no volume flow described below, it turns out that in binary systems there can be only one diffusion coefficient, and thus no Onsager reciprocal relations (63e). The simplest nontrivial case with an Onsager reciprocal relation is ternary diffusion; fortunately, suitable data presently exist for ten such systems. Systems with more components are much more complex; furthermore no adequate diffusion data exist.

A. The TIP description of diffusion (119)

It can be shown (63d) that the entropy production is

$$T\sigma = J_1\left(-\frac{\partial \mu_1}{\partial x_1}\right) + J_2\left(-\frac{\partial \mu_2}{\partial x_2}\right) + J_3\left(-\frac{\partial \mu_3}{\partial x_3}\right) \qquad (69)$$

TABLE 11

Test of equation 67 (gravitational cells)

Salt	t_1^g	t_1^h	Concentration in c or m	References
NaI	0.383	0.375 (18°C.)	0.19 G 0.1 M	G(105), M(34)
KI	0.487	0.489	0.1941	G(107), M(99)
RbI	0.506	0.497 (18°C.)	0.142 G 0.1 M	G(134), M(34)
CsI	0.496	0.497 (18°C.)	0.161 G 0.1 M	G(134), M(34)
HCl	0.85	0.835	1.01	G(35), H(81)
LiCl	0.23	0.245	4.93	G(35), H(89)
NaCl	0.34	0.365	4.25	G(35), H(81)
KCl	0.50	0.486	2.71	G(35), H(106)
$BaCl_2$	0.36	0.379	0.98	G(35), H(90)

where the subscripts 1, 2, and 3 refer to solute 1, solute 2, and the solvent, respectively, J_i refers to the flow, and $\partial\mu_i/\partial x$ refers to the chemical potential gradient. However, the experiments are carried out in such a way that no volume flow occurs; i.e.,

$$J_1\bar{V}_1 + J_2\bar{V}_2 + J_3\bar{V}_3 = 0 \tag{70}$$

where $\bar{V}_i$ is the partial molal volume. Moreover the forces of equation 69 are related by the Gibbs–Duhem equation

$$c_1(\partial\mu_1/\partial x) + c_2(\partial\mu_2/\partial x) + c_3(\partial\mu_3/\partial x) = 0 \tag{71}$$

where c_i is the concentration in moles per liter. Since it was noted previously that the Onsager reciprocal relations are valid only for independent flows and forces, these two secondary conditions can be used to get rid of the dependent solvent terms in $T\sigma$. By simple substitution one obtains

$$T\sigma = J_1Y_1 + J_2Y_2 \tag{72}$$

where

$$Y_i = -\sum_{j=1}^{2}\left[\delta_{ij} + \frac{c_j\bar{V}_i}{c_3\bar{V}_3}\right]\frac{\partial\mu_j}{\partial x} \tag{73}$$

and δ_{ij} is the Kronecker delta. The linear relations are

$$\begin{aligned} J_1 &= L_{11}Y_1 + L_{12}Y_2 \\ J_2 &= L_{21}Y_1 + L_{22}Y_2 \end{aligned} \tag{74}$$

and because the J_i as well as the Y_i are independent, the Onsager reciprocal relation

$$L_{12} = L_{21} \tag{75}$$

should now be valid.

B. COMPARISON WITH FICK'S LAW DESCRIPTION

Ordinarily, diffusion is described by Fick's law. Generalized to ternary systems, Fick's law involves concentration gradients and has the form (3)

$$\begin{aligned} J_1 &= -D_{11}\frac{\partial c_1}{\partial x} - D_{12}\frac{\partial c_2}{\partial x} \\ J_2 &= -D_{21}\frac{\partial c_1}{\partial x} - D_{22}\frac{\partial c_2}{\partial x} \end{aligned} \tag{76}$$

where D_{ij} are the diffusion coefficients in liters per centimeter-second and c_i are concentrations in moles per liter. The D_{ii} are principal or main coefficients. The D_{ij} are the interaction or cross coefficients and are somewhat smaller in numerical value than the D_{12}. Equation 76 is convenient for experiment because concentration gradients are easy to measure. However, D_{12} does *not* equal D_{21} in general.

All the experimental data have been reported in terms of D_{ij}. Therefore, in order to test the Onsager reciprocal relation, it is necessary to get the L_{ij} in terms of the D_{ij}. This is done by expanding $\partial\mu_i/\partial x$ into

$$\frac{\partial\mu_i}{\partial x} = \sum_{j=1}^{2}\frac{\partial\mu_i}{\partial c_j}\frac{\partial c_j}{\partial x} \tag{77}$$

substituting equation 77 into the Y_i of equation 75, and comparing the corresponding coefficients of $\partial c_i/\partial x$ in equations 74 and 76. From the four resulting expressions for D_{ij} one solves for the L_{ij} and obtains

$$\begin{aligned} L_{11} &= \frac{dD_{11} - bD_{12}}{ad - bc} & L_{12} &= \frac{aD_{12} - cD_{11}}{ad - bc} \\ L_{21} &= \frac{dD_{21} - bD_{22}}{ad - bc} & L_{22} &= \frac{aD_{22} - cD_{21}}{ad - bc} \end{aligned} \tag{78}$$

where

$$\begin{aligned} a &= \left[\left(1 + \frac{c_1\bar{V}_1}{c_3\bar{V}_3}\right)\frac{\partial\mu}{\partial c_1} + \frac{c_2\bar{V}_1}{c_3\bar{V}_3}\frac{\partial\mu_2}{\partial c_1}\right] \\ b &= \left[\frac{c_1\bar{V}_2}{c_3\bar{V}_3}\frac{\partial\mu_1}{\partial c_1} + \left(1 + \frac{c_2\bar{V}_2}{c_3\bar{V}_3}\right)\frac{\partial\mu_2}{\partial c_1}\right] \end{aligned} \tag{79}$$

and c and d are the same respectively as a and b except that $\partial/\partial c_1$ is replaced by $\partial/\partial c_2$. Nowhere in the above argument have the Onsager reciprocal relations been assumed. From equations 78, the necessary and sufficient condition for the Onsager reciprocal relation to be valid is

$$\begin{aligned} aD_{12} + bD_{22} &= cD_{11} + dD_{21} \\ ad - bc &\neq 0 \end{aligned} \tag{80}$$

To get the L_{ij} or to verify the Onsager reciprocal relation, one must know c_i, $\bar{V}_i$, D_{ij}, and $\partial\mu_i/\partial c_j$. These quantities are readily available for the ten ternary diffusion systems except for the thermodynamic quantity $\partial\mu_i/\partial c_j$. Unfortunately no thermodynamic data are available in the proper concentration ranges for nine of the systems, and as a result, the activity coefficients and their derivatives with concentration had to be estimated (44, 118, 119).

C. THE TEST OF THE ONSAGER RECIPROCAL RELATION

The following systems were investigated at the concentrations indicated:

I. LiCl(0.25)–KCl(0.2)–H_2O (43, 57)
II. LiCl(0.25)–NaCl(0.2)–H_2O (43, 57)
III. NaCl(0.25)–KCl(0.25)–H_2O (123)
IV. NaCl(0.5)–KCl(0.25)–H_2O (123)
V. NaCl(0.25)–KCl(0.5)–H_2O (123)
VI. NaCl(0.5)–KCl(0.5)–H_2O (123)
VII. NaCl(1.5)–KCl(1.5)–H_2O (42)
VIII. Raffinose(0.015)–KCl(0.5)–H_2O (40)
IX. Raffinose(0.015)–KCl(0.1)–H_2O (40)
X. Raffinose(0.015)–urea(0.5)–H_2O (41)

It can be shown (119) that these are ternary diffusion systems even though there are four diffusing species in systems I to IX. System VII is the only one for which thermodynamic data exist.

TABLE 12

Test of equation 80

	I	II	III	IV	V	VI	VII*	VIII	IX	X
Lefthand side of equation 80†	3.73	3.50	3.12	2.19	2.25	1.76	1.10	1.55	1.53	0.41
Righthand side of equation 80†	3.80	3.71	3.24	2.22	2.30	1.80	1.14	1.16	1.53	0.32
Difference	0.07	0.21	0.12	0.03	0.05	0.04	0.04	0.39	0	0.09
Probable error	0.17	0.20	0.12	0.08	0.07	0.05	0.06	0.21	0.27	0.10
L_{12}/L_{21}	1.03	1.14	1.05	1.02	1.04	1.03	1.06	0.42	1.00	0.58

* These values have been calculated from Dunlop's data (42).

† 10^{-8} $\bar{R}T$ has been factored out.

In table 12 are given the right- and lefthand sides of equation 80, the difference between them, and the probable error of the calculation based on the assumed errors in D_{ij} and the activity coefficient estimates. Also included is the quantity L_{12}/L_{21}. Similar results for systems III to VI were given by Dunlop and Gosting (44).

The agreement is within the probable error for all cases except VIII and is remarkably good considering the experimental difficulties of determining D_{ij} and the errors inherent in estimating thermodynamic quantities. (Private correspondence has revealed that the errors in D_{ij} for case VIII were underestimated in the calculations.)

VII. Conduction of Heat and Electricity in Anisotropic Solids

The discussion will be confined to heat conductivity. This case will be considered in some detail, both because it is interesting and because adequate descriptions of the experiments are relatively inaccessible. The equations and interpretation for electrical conductivity are the same, but no suitable electrical experiments have been carried out on crystals.

A. The Classical Equations

The traditional macroscopic theory of heat conduction in crystals is more than 100 years old and is based on a simple generalization of Fourier's law for an isotropic substance (55, 56). Fourier's law is

$$J_i = -k\frac{\partial T}{\partial x_i} \tag{81}$$

where J_i is the component of heat flow along the coordinate axis x_i, and k is the thermal conductivity. It seems intuitively clear that in an anisotropic substance contributions to the component J_1, say, will be made not only from the temperature gradient $\partial T/\partial x_1$, but from the gradients $\partial T/\partial x_2$ and $\partial T/\partial x_3$ as well. Thus classically (13, 25, 145, 148, 156) one writes

$$\begin{aligned} J_1 &= -\left[k_{11}\frac{\partial T}{\partial x_1} + k_{12}\frac{\partial T}{\partial x_2} + k_{13}\frac{\partial T}{\partial x_3}\right] \\ J_2 &= -\left[k_{21}\frac{\partial T}{\partial x_1} + k_{22}\frac{\partial T}{\partial x_2} + k_{23}\frac{\partial T}{\partial x_3}\right] \\ J_3 &= -\left[k_{31}\frac{\partial T}{\partial x_1} + k_{32}\frac{\partial T}{\partial x_2} + k_{33}\frac{\partial T}{\partial x_3}\right] \end{aligned} \tag{82}$$

The array of nine numbers

$$[k_{ij}] = \begin{vmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{vmatrix} \tag{83}$$

is called the thermal conductivity tensor and is a second-rank tensor.

The actual numbers which go into this array depend on how the (orthogonal) axes x_1, x_2, x_3 are chosen with respect to the natural axes of the crystal. This tensor, however, represents a physical property of the crystal; hence values of the conductivity in a given direction do not depend on the coördinate axes to which this direction or the tensor are referred.

For those not too familiar with the concept of a tensor, it can be regarded as a generalization of the concepts of scalar and vector (122b). A scalar (0^{th} rank tensor) does not depend on direction and has no subscripts on its single component. A vector (first-rank tensor) is determined by or is related to one direction and its components have one subscript. A second-rank tensor, such as $[k_{ij}]$, is connected with two directions and has two subscripts. For example, $[k_{ij}]$ is connected with the directions of the vectors

$$\mathbf{J} = (J_1, J_2, J_3)$$

and

$$\mathbf{grad}\ T = \left(\frac{\partial T}{\partial x_1}, \frac{\partial T}{\partial x_2}, \frac{\partial T}{\partial x_3}\right)$$

Higher-rank tensors appear as extensions of the above ideas. A tensor is rigorously defined by transformation relations such as equations 89, 90, and 91 given below.

Our interest is in the symmetry of the thermal conductivity tensor, i.e., whether $k_{ij} = k_{ji}$. There is nothing *a priori* which requires a tensor to be symmetric, although many second-rank ones, such as the magnetic or electric susceptibility tensors, are symmetric. However, the electrical conductivity in a *magnetic field* (Hall effect) and the heat conductivity in a *magnetic field* (Righi-Leduc effect) are represented by nonsymmetric second-rank tensors (see Section VIII,C).

B. THE TIP EQUATIONS

It can be shown quite straightforwardly (63f) that

$$T\sigma = \sum J_i \left(-\frac{1}{T}\frac{\partial T}{\partial x_i} \right) \tag{84}$$

and therefore the linear laws are

$$J_i = -\sum_j \frac{L_{ij}}{T}\frac{\partial T}{\partial x_j} \tag{85}$$

Comparing equation 85 with equation 82, one obtains

$$L_{ij} = Tk_{ij} \tag{86}$$

Thus the Onsager reciprocal relations will be experimentally verified if experiment shows $[k_{ij}]$ to be symmetric.

It is interesting to note that equation 85 is a consequence of the assumptions of the theory of irreversible processes. Since it is of the same form as the generalized form of Fourier's law (equation 82), equation 85 can be regarded as a derivation of Fourier's law from more basic thermodynamic principles.

It may well be asked at this point, does the TIP hypothesis of linear equations actually yield a proper representation of conduction phenomena? For example, if equation 85 is really valid and if the temperature gradients $(\partial T/\partial x_i)$ are changed in sign, then all the J_i should change sign but the value of the conductivity should remain the same. If this were not observed, the form of equation 85 could not be valid, and perhaps a representation with terms in $\partial^2 T/\partial x_i \partial x_j$ or $(\partial T/\partial x_i)^2$ would be necessary. This question (i.e., whether the thermal conductivity tensor is "centrosymmetric") was tested experimentally on an appropriate crystal (tourmaline, point symmetry C_{3v}); when the sign of the gradients was changed the flows *were* reversed and the conductivity *was* found to be the same (86, 147, 151). An appropriate crystal is one whose point symmetry does not already have a center of symmetry.[4]

C. PROPERTIES OF THE THERMAL CONDUCTIVITY TENSOR

As noted earlier, the numerical values of the entries in $[k_{ij}]$ depend on the choice of axes. If the axes coincide with the crystal axes, insofar as this is possible, the tensor may take simpler forms. To obtain a better background for the discussion of the experiments, a very simple procedure for working out these forms is summarized below (160).

Consider a set of orthogonal axes x_1, x_2, x_3. If one wishes to change to a new set of orthogonal axes x_1', x_2', x_3' with the same origin, then the new axes in terms of the old are given by

$$x_i' = \sum_j a_{ij}x_j \tag{87}$$

where a_{ij} is the cosine of the angle between the new axis x_i' and the old axis x_j; i.e., its direction cosine. The a_{ij} can for convenience be put into an array of nine components (not a tensor):

	x		
x'	a_{11}	a_{12}	a_{13}
	a_{21}	a_{22}	a_{23}
	a_{31}	a_{32}	a_{33}

(88)

The transformation of the components of the tensor upon the transformation of axes is directly related to these direction cosines a_{ij}. Thus the components of a first-rank tensor (vector)

$$\mathbf{p} = (p_1, p_2, p_3)$$

transform as

$$p_i' = \sum_j a_{ij}p_j \tag{89}$$

of a second-rank tensor such as $[k_{ij}]$ as

$$k_{ij}' = \sum_{l,m} a_{il}a_{jm}k_{lm} \tag{90}$$

and of a third-rank tensor T_{ijk} as

$$T_{ijk}' = \sum_{l,m,n} a_{il}a_{jm}a_{kn}T_{lmn} \tag{91}$$

and so on.

Consider, for example, a crystal which has only a fourfold axis of symmetry (C_4), and let the x_3 axis be the crystallographic principal axis. The $[k_{ij}]$, as far as is known at this point, has the general form of expression 83. Suppose now the axes are rotated one-fourth of the way around the x_3 axis. The table of direction cosines 88 for this transformation can be seen to be

$$\begin{vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

The new k_{12}' is by simple calculation from equation 90 found to be

$$k_{12}' = -k_{21} \tag{92}$$

But a rotation of the axes by 90° really has not changed anything, since the crystal has a fourfold axis; its properties must be unchanged by a symmetry operation. The new components must therefore be the same as the old; hence $k_{12}' = k_{12}$. By equation 92

$$k_{12}' = k_{12} = -k_{21} \tag{93}$$

[4] There are twenty-one such point symmetries out of the thirty-two total. Of these there are fourteen (including C_{3v}) for which a third-rank term in the direction of one of the conventional coördinate axes changes sign when the temperature gradient in that direction changes sign, and would thus cause different heat conductivities in the forward and reverse directions.

In a similar way

$$k'_{22} = k_{11} = k_{22} \tag{94}$$

and

$$k_{13} = k_{23} = k_{31} = k_{32} = 0 \tag{95}$$

Of course, a system with a fourfold axis automatically has a twofold axis, but the calculations reproduce equation 95. For this example no other symmetry operations remain. Thus a consideration of the symmetry properties of the crystal has reduced the form of the general tensor expression 83 to this much simpler form

$$\begin{vmatrix} k_{11} & k_{12} & 0 \\ -k_{12} & k_{11} & 0 \\ 0 & 0 & k_{33} \end{vmatrix} \tag{96}$$

The more symmetrical the crystal, the greater is this simplification. In the example it is seen that considerations of geometrical symmetry alone have resulted in

$$k_{13} = k_{31} \qquad k_{23} = k_{32} \tag{97}$$

quite independently of any possible existence of the Onsager reciprocal relations.

It turns out that all the orthorhombic (C_{2v}, D_2, D_{2h}), all the cubic (T, T_d, T_h, O, O_h), and certain trigonal (D_3, C_{3v}, D_{3d}), hexagonal (D_6, C_{6v}, D_{3h}, D_{6h}), and tetragonal (D_4, C_{4v}, D_{2d}, D_{4h}) crystal classes satisfy

$$k_{ij} = k_{ji} \tag{98}$$

for *all* i and j by *geometrical symmetry considerations alone*. Therefore a test of the Onsager reciprocal relations must come from consideration of the remaining classes; namely, the triclinic (C_1, C_i), monoclinic (C_2, C_s, C_{2h}), and these of the trigonal (C_3, C_{3i}), tetragonal (C_4, S_4, C_{4h}), and hexagonal (C_6, C_{3h}, C_{6h}) classes.

The simplest nontrivial cases are those of the above trigonal, tetragonal, and hexagonal systems, all of which have exactly the same form of tensor; namely, expression 96. Henceforth only crystals with this type of tensor will be considered. Clearly, it can be symmetric only if $k_{12} = 0$. Thus if experiment shows that k_{12} does equal zero, it has been shown that the Onsager reciprocal relations are experimentally satisfied for that crystal.

D. THE EXPERIMENTS OF SORET AND VOIGT

The experiments carried out to determine whether $[k_{ij}]$ is symmetric are interesting and rather clever.

Soret's experiments (143, 144, 146) are all based on heating a point of a thin crystal plate. Heat will flow away from this point, and the temperature gradient will give rise to a family of isothermals. In an isotropic crystal these isothermals are circles; in anisotropic systems, the isothermal lines are ellipses in general (13, 25, 122c, 145, 156).

First, consider a thin plate very large in extent (or alternatively surrounded by a circular bounding surface of highly conducting material) which is cut perpendicular to the principal axis (x_3) of a crystal whose tensor is like expression 96 (144). In this case, it can be shown that on heating the center, the resulting isothermals are always circles. If the tensor is symmetric, the flow of heat will be in straight lines away from the center; if not, the heat will flow away in spirals (figure 4) (13, 25, 122c, 156). Suppose now a very thin sector is cut out of the plate. If the tensor is not symmetric, the spiral heat flow will result in an accumulation of heat on one side of the cut and a loss on the other. One would thus find a temperature difference between the two sides. Soret (144) observed no such difference. The analogous experiment for electrical conductivity in a magnetic field (Hall effect), where $k_{12} \neq 0$, was suggested independently by Boltzmann (9) and carried out by Ettinghausen and Nernst (49).

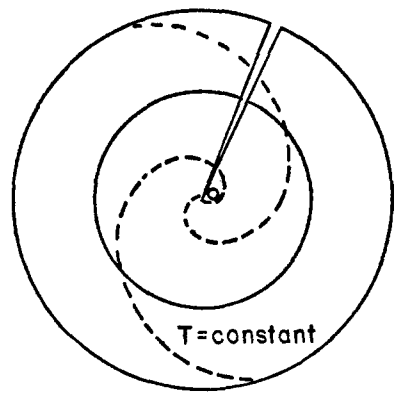

FIG. 4. Circular plate cut perpendicular to the axis x_3 heated at center O. If the tensor 96 is not symmetric, heat flow (dotted lines) will be in spirals.

Secondly, consider heating on an edge a very large but thin rectangular piece also cut perpendicular to the principal axis. In this case, spiral heat flow results in isotherms which are not symmetric about the heating point (143, 144). The effect is magnified by sawing such a piece in half, rotating one of the halves about an axis perpendicular to the saw cut but leaving a small space between the pieces, and heating a point in the crack between the two pieces (figure 5). When the appropriate crystals were used, Soret observed no discontinuity in the isotherms (143, 144).

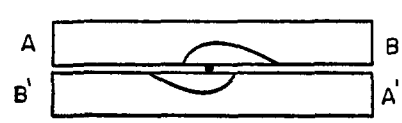

FIG. 5. Thin plate of crystal cut perpendicular to the principal axis x_3 and sawed in half. One half is rotated with respect to the other about an axis perpendicular to the saw cut. Thus originally edges A and A′ were continuations of each other. The two plates are separated by a small space, so that no heat is transferred from one plate to the other. The plates are heated at O, and if the tensor 96 is asymmetric, the isotherms will exhibit a discontinuity.

The isotherms are made visible in this way (161). The plates are covered with a thin layer of melted wax, which is allowed to solidify. When the point is heated, the wax will melt in the region where the temperature is higher than its freezing point. The boundary line between melted and solid wax is the isothermal corresponding to the freezing temperature. When the melted wax is allowed to cool, this isothermal becomes visible as a raised edge.

Third, consider a large thin piece this time cut parallel to the principal axis. If the plate is heated at an interior point near the middle, the heat flow results in elliptical isotherms which are unsymmetric with respect to that diameter which is parallel to the principal axis (144, 146). By means of the wax technique, the isotherm is made visible and is viewed with an ocular micrometer. Upon rotating the sample 180° about the heating point, Soret found that deviations from perfect symmetry appeared to be about one-fortieth of the diameter (146). However, such deviations were also observed with isotropic substances where no such dissymmetry could occur. Since the diameter is inversely proportional to the square root of conductivity along the principal axis, he concluded that for crystals of gypsum, dolomite, erythrite, and apatite the tensor was symmetric within his experimental error (5 per cent).

Voigt's experiment (155), suggested also by P. Curie (30), is more direct and more accurate. Suppose a fixed temperature difference is applied to the ends of a long, narrow, thin plate of a crystal whose tensor is like expression 96. Let the axis x_1 be along the length, x_2 along the width, and the principal axis x_3 be perpendicular to the plate (figure 6). The solution of the

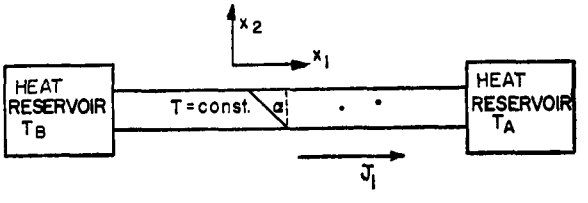

FIG. 6. Schematic diagram of the Curie–Voigt experiment. The principal axis x_3 comes out of the paper. If the tensor 96 is asymmetric, the isothermal lines far from the region of end effects will be inclined away from the normal (dotted line) to the direction of heat flow.

boundary value problem is independent of the symmetry of the tensor and shows that the heat flows only along x_1. Hence for this case

$$J_1 = -k_{11}\frac{\partial T}{\partial x_1} - k_{12}\frac{\partial T}{\partial x_2}$$

$$0 = J_2 = +k_{12}\frac{\partial T}{\partial x_1} - k_{11}\frac{\partial T}{\partial x_2} \qquad (99)$$

$$0 = J_3 = -k_{33}\frac{\partial T}{\partial x_3}$$

Consequently from the expression for J_2, one obtains

$$\frac{\partial T}{\partial x_2}\Big/\frac{\partial T}{\partial x_1} = k_{12}/k_{11} = \tan\alpha \qquad (100)$$

where α is the angle which the isothermal straight line makes with the normal to the line of heat flow (see figure 7). By means of the melting wax technique, an

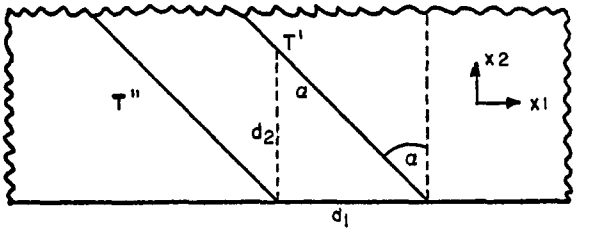

FIG. 7. Expanded drawing of isothermals to show how α is related to the thermal gradients. Since $(\partial T/\partial x_1) = (T''' - T')/d_1 = \Delta T/(d_2 \tan\alpha)$ and $\partial T/\partial x_2 = \Delta T/d_2$, clearly

$$\left(\frac{\partial T}{\partial x_2}\right)\Big/\left(\frac{\partial T}{\partial x_1}\right) = \tan\alpha$$

isothermal is located. If this line is inclined away from the normal, then the tensor is not symmetric, and the ratio of k_{12} to k_{11} is given by equation 100.

Owing to possible heat losses from the edges, it is more precise to use Voigt's "twin plate" method. The plate is sawed in half along the x_1 axis, one piece is rotated about the x_2 axis, and the two pieces are clamped together. If the tensor is asymmetric, the isotherms will have the form shown in figure 8. One meas-

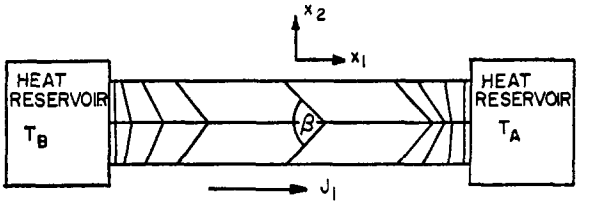

FIG. 8. Schematic diagram of Voigt's twin-plate experiment. If the tensor 96 is not symmetric, the isothermals will form a V symmetric along the x_1 axis with an interior angle β. If symmetric, the isothermals are perpendicular to the x_1 axis.

ures the angle β at the common edge near the middle, which avoids any distortion due to losses at the edges or due to end effects. The angle α is $[90° - (\beta/2)]$. Voigt (155) found that for suitable crystals of apatite and dolomite, the lines were straight and perpendicular to x_1. More precisely, β was 180° with an error of not more than 4 min. (i.e., <0.037 per cent). Therefore, α is less than 2′, and

$$k_{12}/k_{11} < 0.0005$$

This value implies that $k_{12} = 0$ to less than 0.05 per cent and consequently that the tensor *is* symmetric.

E. REPLY TO CASIMIR'S OBJECTION

An objection to the conclusions drawn from these experiments has been raised by Casimir (26, 122d): namely, that the individual heat flows are not observable physical quantities, but only their divergence (net flow) is. Consequently one could add a divergence-free tensor $[d_{ij}]$ to $[k_{ij}]$ without altering any observable quantity. A sufficient condition for a divergence-free tensor is that it be antisymmetric, i.e., of the form (for second rank)

$$\begin{vmatrix} 0 & d_{12} & d_{13} \\ -d_{12} & 0 & d_{23} \\ -d_{13} & -d_{23} & 0 \end{vmatrix}$$

Now it can be easily shown that a nonsymmetric tensor can be split up into the sum of a symmetric and an antisymmetric tensor, and, conversely, the addition of an antisymmetric tensor to a symmetric one yields a nonsymmetric tensor. Therefore it was argued that nothing can be determined about the symmetry properties of the thermal conductivity tensor from the experiments cited, because only the divergence is observable and because the addition of the antisymmetric $[d_{ij}]$ could make the sum $[d_{ij} + k_{ij}]$ nonsymmetric irrespective of whether $[k_{ij}]$ is symmetric.

However, it should be noted that the solution of the boundary value problem is independent of the tensor's symmetry or lack of it (25). Therefore the form of equations 99 is valid whether or not a divergence-free tensor is added. But in Voigt's experiments (as also in Soret's), no flow is measured. The observable quantity is the isothermal line, not a divergence, and Casimir's objection is not relevant. Thus one concludes that the above experiments do exactly what they were designed to do; i.e., they test the asymmetry of the conductivity tensor. It might be mentioned that the same type of experiments was successful in showing the nonsymmetrical character of the Hall tensor (49).

It is concluded that the experiments of Soret and of Voigt have shown that $[k_{ij}]$ is symmetric, and thus by equation 86 the Onsager reciprocal relations are verified experimentally for heat conduction in anisotropic solids.

VIII. THERMOMAGNETISM AND GALVANOMAGNETISM

This detailed review of the experimental evidence for the Onsager reciprocal relations will be concluded with a discussion of galvanomagnetic and thermomagnetic effects (11, 24, 85, 111a), which ordinarily are not too well known to chemists. The most familiar one is the Hall effect, but there are a large number which could be defined (51, 54). We shall be primarily interested in the Ettinghausen and Ettinghausen–Nernst effects, because these, together with the thermal conductivity, can be related to each other by an Onsager reciprocal relation. The relation was originally derived by Bridgman (16b) in an incorrect way, analogous to the one used by Kelvin to derive equation 20.

A. THE GENERAL TIP EQUATIONS FOR THERMOGALVANOMAGNETISM

1. $T\sigma$

In the general case of simultaneous heat and electrical flow in a magnetic field, it is necessary to consider all three coördinate directions. For this case it can be shown (21, 22, 23, 51, 52, 53, 63g, 110) that $T\sigma$ may be written in vector form as

$$T\sigma = \mathbf{J}\cdot T\,\mathbf{grad}(1/T) + \mathbf{I}\cdot\mathbf{E} \tag{101}$$

where $\mathbf{E} = -\mathbf{grad}\,\phi$, $\mathbf{I}$ is the electrical current, and the use of boldface type represents vectors. In component form, equation 101 is

$$T\sigma = J_x G_x + J_y G_y + J_z G_z + I_x E_x + I_y E_y + I_z E_z \tag{102}$$

where

$$G_x = T\frac{\partial(1/T)}{\partial x} = -\frac{1}{T}\frac{\partial T}{\partial x} \text{ and } E_x = -\frac{\partial\phi}{\partial x}, \text{ etc.}$$

It should be noted that $\mathbf{E}$ may be employed only in the case of a metal. Otherwise a term involving the chemical part of the electron chemical potential is required (21, 22, 23, 51, 52, 53, 54). It is interesting to note that the magnetic field does not appear explicitly in these equations.

2. *The linear laws and Onsager reciprocal relations*

In the standard way, the flows may be written as a linear function of the forces. It is convenient to write them in vector and tensor form as follows:

$$\begin{aligned} \mathbf{I} &= L_{ee}\mathbf{E} + L_{eq}\mathbf{G} \\ \mathbf{J} &= L_{qe}\mathbf{E} + L_{qq}\mathbf{G} \end{aligned} \tag{103}$$

where $\mathbf{G} = \mathrm{T}\,\mathbf{grad}\,(1/T)$. The L's are clearly second-rank tensors and are functions of the magnetic induction B. In particular, L_{ee} is the electrical conductivity (Hall) tensor, L_{qq} is the heat conductivity tensor, and the L_{eq} and L_{qe} are related to longitudinal and transverse thermoelectric effects in a magnetic field.

The Onsager reciprocal relations for this case are given in component form by equation 10. In tensor form they become

$$\begin{aligned} L_{ee}(\mathbf{B}) &= L_{ee}^{\dagger}(-\mathbf{B}) \\ L_{qq}(\mathbf{B}) &= L_{qq}^{\dagger}(-\mathbf{B}) \\ L_{eq}(\mathbf{B}) &= L_{qe}^{\dagger}(-\mathbf{B}) \end{aligned} \tag{104}$$

where the dagger refers to the transposed tensor. The need for the transposed notation to express the Onsager reciprocal relations is seen by writing out equation 103 in component form.

3. A more convenient form

(a) The transformed linear laws

Experimentally it is more convenient to deal with currents and temperature gradients, and therefore the use of **I** and **G** as independent variables will simplify the definitions of the effects of interest. The desired equations

$$\begin{aligned} \mathbf{E} &= l_{ee}\mathbf{I} + l_{eq}\mathbf{G} \\ \mathbf{J} &= l_{qe}\mathbf{I} + l_{qq}\mathbf{G} \end{aligned} \tag{105}$$

are obtained by writing equations 103 in component form, solving for the components of **E**, and collecting the proper terms. Alternatively, the inversion could be carried out by matrix methods (23).

Suppose that the experimental conditions are such that **B** is parallel to the z axis and that **I** and **G** are restricted to the xy plane. Then in component form equation 105 is written

$$\begin{aligned} E_x &= l_{11}I_x + l_{12}I_y + l_{13}G_x + l_{14}G_y \\ E_y &= l_{21}I_x + l_{22}I_y + l_{23}G_x + l_{24}G_y \\ J_x &= l_{31}I_x + l_{32}I_y + l_{33}G_x + l_{34}G_y \\ J_y &= l_{41}I_x + l_{42}I_y + l_{43}G_x + l_{44}G_y \end{aligned} \tag{106}$$

(b) The transformed Onsager reciprocal relations

When the Onsager reciprocal relations (equations 104) are applied to the expressions for l_{ij} in terms of the L_k, it is found that

$$\begin{aligned} l_{ee}(\mathbf{B}) &= l^{\dagger}_{ee}(-\mathbf{B}) \\ l_{qq}(\mathbf{B}) &= l^{\dagger}_{qq}(-\mathbf{B}) \\ l_{eq}(\mathbf{B}) &= -l^{\dagger}_{qe}(-\mathbf{B}) \end{aligned} \tag{107}$$

Conversely, the validity of equations 107 implies the validity of equations 104. Equations 107 are therefore the Onsager reciprocal relations for the linear laws (equations 105).

B. THE ISOTROPIC METAL

1. Form of the tensor with and without the field

Consider an isotropic metal. In the absence of a field, it can be shown by the same kind of geometrical symmetry arguments used in Section VII that the tensor of equations 106 has the form

$$l(B=0) = \begin{vmatrix} l_{11} & 0 & l_{13} & 0 \\ 0 & l_{11} & 0 & l_{13} \\ l_{31} & 0 & l_{33} & 0 \\ 0 & l_{31} & 0 & l_{33} \end{vmatrix} \tag{108}$$

where l_{11} is the resistance, l_{33} the thermal conductivity, and l_{13} and l_{31} are related to the *absolute* thermoelectric power and the *absolute* Peltier coefficient, respectively. For example, for the junction of two isotropic metals a and b, $\Pi = l^a_{31} - l^b_{31}$ (122e).

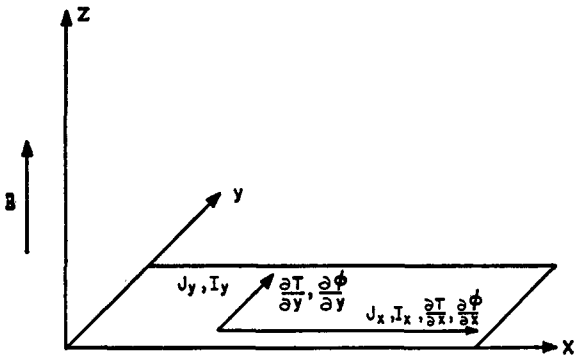

FIG. 9. Schematic diagram of an isotropic metal in a magnetic field. The field is directed along the z axis, and x is chosen as the direction of the primary currents. The metal is isotropic only in the xy plane in a non-zero field.

Suppose now that a magnetic field is directed along the z axis as shown in figure 9. Then in a sense the metal is no longer isotropic, since z is now a unique direction. However there is still isotropy in the xy plane. Since systems with a three-, four-, or sixfold z axis are also isotropic in the xy plane, the four pieces of l—l_{ee}, l_{qq}, l_{eq}, and l_{qe}—each take exactly the same form as expression 96, with the z ($= x_3$) components omitted. Thus

$$l(B) = \begin{vmatrix} l_{11} & l_{12} & l_{13} & l_{14} \\ -l_{12} & l_{11} & -l_{14} & l_{13} \\ l_{31} & -l_{41} & l_{33} & l_{34} \\ l_{41} & l_{31} & -l_{34} & l_{33} \end{vmatrix} \tag{109}$$

Because of the isotropy (21, 51, 54, 79) l_{12}, l_{14}, l_{41}, and l_{34} must be odd functions of B, i.e., $l_{ij}(-B) = -l_{ij}(B)$, and l_{11}, l_{33}, l_{13}, and l_{31} must be even functions of B, i.e., $l_{kl}(-B) = l_{kl}(B)$.

2. The Onsager reciprocal relations

Owing to the assumed symmetry, a number of the Onsager reciprocal relations are redundant. However there are still two independent ones arising from the l_{eq} and l_{qe} pieces of l. From equations 107 and because l_{13} and l_{31} are even and l_{14} and l_{41} are odd, one finds that

$$l_{13}(B) = -l_{31}(-B) = -l_{31}(B) \tag{110}$$

$$l_{14}(B) = -l_{41}(-B) = l_{41}(B) \tag{111}$$

The Bridgman equation is related to equation 111, and equation 110 is the Kelvin thermoelectric equation for absolute Peltier and thermoelectric coefficients in a magnetic field (85).

C. EXPERIMENTAL DEFINITIONS OF THE DESIRED EFFECTS

The Bridgman equation relates the Ettinghausen and Ettinghausen–Nernst effects to the thermal conductivity. By means of Fieschi's definitions (51, 54), the desired coefficients are given in terms of the l_{ij} without appeal to the Onsager reciprocal relations. Other definitions (21, 22, 23, 85, 110) are the same except for sign or a factor B.

The (isothermal) thermal conductivity k_i is defined as

$$k_i \equiv \frac{-J_x}{\frac{\partial T}{\partial x}} = \frac{J_x}{TG_x} \qquad I_x = I_y = G_y = 0 \tag{112}$$

and by equations 109

$$k_i = l_{33}/T \tag{113}$$

The definition is clearly the same if one chooses the y direction. The label "isothermal" is necessary because an "adiabatic" heat conductivity can be defined for which $I_x = I_y = J_y = 0$ (21, 22, 23, 51, 54, 85, 110).

The Ettinghausen effect is the appearance of a temperature gradient in the y direction when a current flows in the x direction. The Ettinghausen coefficient P^t is

$$P^t \equiv \frac{(\partial T/\partial y)}{I_x} = \frac{-TG_y}{I_x} \qquad I_y = J_y = G_x = 0 \tag{114}$$

whence

$$P^t = \frac{l_{41}T}{l_{33}} \tag{115}$$

The Ettinghausen–Nernst effect is the appearance of a potential gradient in the y direction when heat flows in the x direction. The (isothermal) Ettinghausen–Nernst coefficient Q_i^t is defined as

$$Q_i^t \equiv \frac{E_y}{\frac{\partial T}{\partial x}} = -\frac{E_y}{TG_x} \qquad I_x = I_y = G_y = 0 \tag{116}$$

whence

$$Q_i^t = \frac{l_{14}}{T} \tag{117}$$

Although pure heat conduction in a magnetic field is not a part of the Bridgman equation, it is of interest because of its connection with the discussion of Section VII. The Righi–Leduc effect is the appearance of a temperature gradient in the y direction when heat flows only in the x direction. The appropriate coefficient S is defined by

$$S \equiv \frac{\partial T/\partial y}{\partial T/\partial x} = \frac{G_y}{G_x} \qquad I_x = I_y = J_y = 0 \tag{118}$$

whence

$$S = \frac{l_{34}}{l_{33}} \tag{119}$$

But this definition corresponds exactly to Voigt's experiment (Section VII,D), S being the tan α of equation 100. Thus S, the measure of the *asymmetry* of the heat conductivity tensor in a magnetic field, can be determined by the same technique used to show the *symmetry* of the tensor in the absence of the field.

D. THE BRIDGMAN RELATION AND THE EXPERIMENTAL EVIDENCE

From equations 113, 115, and 117 it is immediate that

$$P^t k_i = l_{41} \tag{120}$$

$$TQ_i^t = l_{14} \tag{121}$$

If the Onsager reciprocal relation (equation 111) is valid, then the Bridgman relation

$$P^t k_i = TQ_i^t \tag{122}$$

is valid. Conversely, the validity of the Bridgman relation entails the validity of $l_{14} = l_{41}$.

In table 13 are the values of Q_i^t and $(P^t k_i)/T$ (11, 111a, 142). Unfortunately the experiments are quite difficult, and the results differ from sample to sample, as was found in the thermoelectric and electrokinetic cases. Except for Little's measurements on arsenic (95), there are no cases where all three measurements were done on the same sample (142). In most of the entries in the table the thermal conductivity was the one not directly measured. Perhaps for these reasons the Onsager reciprocal relation (equation 111) is not satisfied quite as well as in the previous examples. Optimistically it could be said that considering the difficulty of the experiments and their attendant errors, the Onsager reciprocal relation is satisfied, especially since the only really appropriate case (Little's data for arsenic) gives almost perfect agreement. Pessimistically it could be said that the validity of the Onsager reciprocal relation

TABLE 13

Test of the Bridgman relation

Substance	$10^{12} \times \frac{P^t k_i}{T}$	$10^{12} \times Q_i^t$	$\frac{P^t k_i}{Q_i^t T}$		Reference
Ag	2.2	1.8	1.22	(1.34)	(154)
Al	0.60	0.42	1.43	(1.8)	(154)
As	22.0	22.5	0.98		(95)
Au	1.2	1.8	0.66	(0.67)	(66)
Bi	2200	2340	0.94	(2.9)	(162)
Cd	0.9	1.2	0.75	(0.76)	(154)
Co	22.0	21.9	1.00		(66)
Cu	2	1.9	1.05	(0.76)	(154)
			0.86		(67)
Fe	8.6	9.5	0.91	(0.88)	(154)
Ni	22.0	30.4	0.72	(3.4)	(66)
Pd	4.00	3.26	1.23	(0.82)	(66)
			1.23		(67)
Sb	220	176	1.25	(0.66)	(162)
Zn	1.00	0.73	1.37	(4.2)	(154)
PbSe–1*	6.2	2.3	2.7		(133)
PbSe–2*	4.5	4.5	1.00		(133)
PbTe–1*	19	13	1.46		(133)
PbTe–2*	3.5	3.5	1.00		(133)

$P^t k_i/T$ and Q^t_i are in volts per gauss degree. The data and references are primarily taken from Borelius' collection (11). The values of $P^t k_i/Q_i^t T$ in parentheses are from a similar collection by Meissner (111a). A crude calculation of l_{41}/l_{14} from the *adiabatic* quantities for iron and nickel (20) gives the values 0.28 and 0.27, respectively.

* The units of $P^t k_i/T$ and Q^t_i are in 10^2 cm.^{2} sec.$^{-1}$ deg.$^{-1}$ The heat conductivities were estimated from a Peltier heat measurement.

is quite probable, but awaits a series of precise measurements on single samples for verification.

It should be emphasized that only one of the Onsager reciprocal relations is tested by the Bridgman equation. The other one, $l_{13} = -l_{31}$, is strictly analogous to equation 20 and must be checked through longitudinal thermoelectric and Peltier measurements in a transverse magnetic field. Although a few such measurements have been made, there are no recent ones (85). The comparisons of Peltier heats and thermoelectric powers obtained by different workers are discordant, and there seem to be only the measurements of Houlliwegue (80) on iron in which both experiments were done on the same sample (24a, 111b). Here the agreement was within 5 per cent.

IX. Cases with Meager or Inconclusive Evidence

Six quite different types of irreversible phenomena have been discussed in some detail above. There are two more for which the evidence is meager or inconclusive and which will be mentioned very briefly.

A. Chemical Reactions

The first case, chemical reactions, is the only common one where the linear laws do not hold in a useful range of deviations from equilibrium. Consequently, the hypothesis of the fundamental assumption (Section II, B,3) is not satisfied. However, sufficiently close to equilibrium it would be expected that linear laws should be valid, and this was in fact shown by Prigogine, Outer, and Herbo (131). Hence near equilibrium, a test of the Onsager reciprocal relations becomes meaningful. The first nontrivial Onsager reciprocal relation comes from a consideration of a triangular chemical reaction system (32b, 125), and it can be shown that the Onsager reciprocal relation is equivalent to the well-accepted principle of detailed balance (32b, 125). It can also be shown that if the Onsager reciprocal relation (detailed balance) is not satisfied, then such a reaction system will exhibit oscillations in the concentrations of its components as it comes to equilibrium. (See, however, the recent discussions in references 1, 2A, 69, 74, and 141.) The experimental studies of this phenomenon, however, have been inconclusive (2A, 140), and the question is still open from an experimental standpoint.

B. Thermomechanical Effects

The second case is the interaction of heat and matter flows in a one-component system (62, 63h, 132b). The two experimental effects are the thermomolecular pressure difference (TPD) and the mechanocaloric effect (MCE), which are defined as follows (132b): Consider a one-component fluid in two vessels connected by a slit or capillary. If there is a temperature difference between the vessels, a flow J_m will result and a pressure difference will be set up. In the steady state $J_m = 0$ and the quantity $(dP/dT)_{J_m=0}$ is the thermomolecular pressure difference. A related quantity is the amount of heat J_q necessary to maintain the system at constant temperature when the fluid is forced through the slit by a pressure difference. This quantity, $(J_q/J_m)_{\Delta T=0}$, is the mechanocaloric effect. It can be shown (132b) that

$$\left(\frac{dP}{dT}\right)_{J_m=0} = \frac{Q_{21}^*}{TV} \tag{123}$$

$$(J_q/J_m)_{\Delta T=0} = Q_{12}^* \tag{124}$$

where Q_{ij}^* (heat of transfer) $= L_{ij}/L_{22}$. Since dP/dT can be obtained from vapor pressure measurements and Q_{12}^* from calorimetric measurements, it is possible in principle to verify the Onsager reciprocal relation. The first measurements of these quantities were carried out on liquid helium II by Kapitza (91) and Meyer and Mellink (115) who stated, without giving numerical comparisons, that to within a few per cent $Q_{12}^* = Q_{21}^*$ (and thus $L_{12} = L_{21}$). More recent data, obtained by Brewer and Edwards (15A) from 1.1 to 1.7°K., are shown in figure 10. Clearly Q_{12}^* and Q_{21}^* are equal within about 5 to 8 per cent, which is the scatter of the data for each type of experiment.

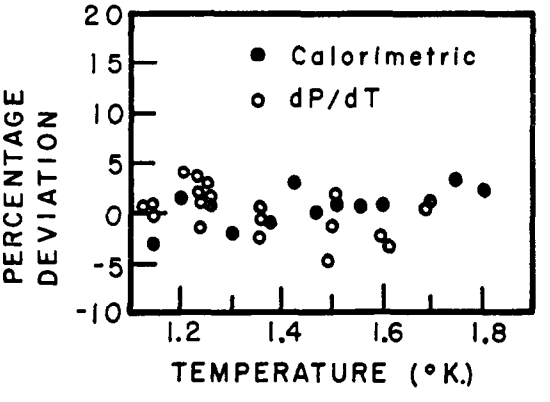

FIG. 10. Plot of Q_{ij}^* for liquid helium II, adapted from figure 3 of reference 15A. Closed circles represent Q_{12}^* (calorimetric) and open circles Q_{21}^* (dP/dT). The per cent deviation is from a theoretical calculation of Q_{ij}^* which is not relevant to this discussion.

X. Assessment

By means of the data in the foregoing sections, it has been possible to check the validity of the Onsager reciprocal relations. The results may be summarized as follows: For thermoelectricity, electrokinetics, isothermal diffusion, and anisotropic heat conduction, the experimental checks are sufficiently good that the validity of these relations is practically unquestionable. With electrolytic transference, most systems check pretty well, i.e., within about 10 per cent. In the remaining ones the experimental errors are too large to yield a significant test, even though equations 67 and 68 are satisfied within these errors. In the thermo-

galvanomagnetic case, the Bridgman relation is nicely verified for the only system where all the quantities were measured on the same sample. With the other systems, the values of l_{41}/l_{14} are more scattered but still reasonably close to 1, i.e., 1 ± 0.5. Because it is most likely that the scatter is a result of not doing all measurements on the same sample, the validity of the Onsager reciprocal relation (equation 111) may be accepted with considerable confidence. With the thermomechanical effects the experimental test is very good, but there are data for only one system. Finally, for chemical reactions, the evidence is inconclusive.

In view of the above, the author concludes that the experimental evidence is overwhelmingly in favor of the validity of the Onsager reciprocal relations. Moreover, this experimental check of the relations is at the same time a proof of both the essential correctness of the linearity assumption and the adequacy of the thermodynamic description of these irreversible phenomena.

It would of course be desirable to have some further experiments to clinch the argument in those cases where experimental errors were especially large. The following are suggested: (*a*) Accurate measurements of Hittorf (or moving boundary) and cell transference numbers in relatively concentrated solutions of weak electrolytes such as cadmium bromide; because of ion association L_{12} and L_{21} will be significantly larger. (*b*) A series of measurements by modern techniques of the three thermogalvanomagnetic coefficients and of the longitudinal Peltier heats and thermoelectric powers in a transverse field to check equations 110 and 111, respectively; all quantities to be determined on the *same* sample. Since semiconductors often have large galvanomagnetic effects, such systems would be most suitable. (*c*) Some direct calorimetric measurements of the heat of transport to compare with the value obtained from the thermomolecular pressure difference on systems other than helium II. Both measurements of course should be made using the same diaphragm. (*d*) A careful reinvestigation of the question of oscillating concentrations in triangular chemical reactions.

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