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*On the Laws of Irreversible Phenomena.* By Dr. LADISLAS NATANSON, Professor of Natural Philosophy in the University of Cracow\*.

IT can scarcely be doubted that the theory of dissipation of energy is still in its infancy. Reversible phenomena are well understood, but they do not involve dissipation at all; and what is known about irreversible phenomena is merely the qualitative aspect of their general laws. In fact, of the general quantitative laws of irreversible phenomena we are as yet utterly ignorant. Now I venture to think there is a general principle underlying irreversible phenomena which is easily seen to be consistent with fact in various cases well investigated: it is an extension of Hamilton's Principle, and (with much diversity, of course, as to form and generality) has been stated by Lord Rayleigh †, by Kirchhoff ‡, by v. Helmholtz §, and by M. Duhem ||. It seems that propo-

\* From the *Bulletin International de l'Académie des Sciences de Cracovie*, Mars 1896.

† Proceedings of the London Mathematical Society, June 1873. 'The Theory of Sound,' i. p. 78 (1877).

‡ *Vorlesungen über Math.-Physik. Mechanik*, 1876, Vorlesung xi.

§ *Borchardt-Crelle's Journal f. Mathematik*, Bd. c. (1886); *Wissenschaftliche Abhandlungen*, Bd. iii. p. 203; *ibid.* Bd. ii. p. 958; Bd. iii. p. 119.

|| *Journal de Mathématiques de Liouville-Jordan* (4) vol. viii. p. 269 (1892); vol. ix. p. 293 (1893); vol. x. p. 207 (1894). See further, Prof. J. J. Thomson's 'Applications of Dynamics to Physics and Chemistry,' London, 1888, where the fundamental standpoint is a very similar one, the chief object of investigation being, however, the theory of reversible phenomena.

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sitions equivalent to those indicated by these investigators could be enunciated in the form of a simple and very general formula; we venture to think that the fundamental principle which it embodies is worth attention. Besides, it seems to afford the proper foundation for an attempt to arrive at some deeper insight into the laws of dissipation of energy.

### PART I.

§ 1. *Introductory.*—Conceive a system: it may be either finite or infinitely small; it may be an independent system, or it may be only a part of some other system. Let the state of the system, at time  $t$ , be determined by the values of certain variable quantities,  $q_i$ , and of their first differential coefficients with respect to the time,  $s_i$  or  $dq_i/dt$ . We shall suppose that the energy of the system consists of two parts, the first of which,  $T$ , is a function of the  $q_i$  and the  $s_i$ , homogeneous of the second degree with respect to the  $s_i$ , and the second, say  $U$ , is a function of the  $q_i$  only. Let  $\mathfrak{S}$  denote the absolute temperature of the system:  $\mathfrak{S}$  may be an independent variable, or otherwise it must be a definite function of the variables. Suppose that the quantities  $q_i, s_i$  received certain arbitrarily chosen infinitesimal increments  $\delta q_i, \delta s_i$ ; the energy  $T$  will then become  $T + \delta T$ , and  $U$  will become  $U + \delta U$ . Let then  $\Sigma P_i \delta q_i$  be the work done on the system reversibly, during the transformation, by extraneous forces, and let  $\delta Q$  or  $\Sigma R_i \delta q_i$  be the quantity of heat simultaneously absorbed by the system from the exterior;  $P_i$  will then be the generalized or Lagrangian extraneous "force" in the "direction" of the variable  $q_i$ , and  $R_i$  will be the "caloric coefficient," as it is called by M. Duhem, or the generalized "thermal capacity" of the system with respect to the variable  $q_i$ .

With respect to the quantity  $\delta Q$  we now make the following assumption, which we shall find is in accordance with fact. Let us suppose that every variation  $\delta q_i$  takes the special value  $dq_i$  or  $s_i dt$ ; then the values of the variables  $q_i$  will become  $q_i + dq_i$ ; the energies  $T$  and  $U$  will become  $T + dT, U + dU$ ; the work done by external forces will be  $\Sigma P_i dq_i$ ; and the quantity of heat absorbed will be  $dQ$  or  $\Sigma R_i dq_i$ . If now the variables be allowed to return to their primitive values  $q_i, T$  and  $U$  will resume their former values  $T, U$ , the external work  $-\Sigma P_i dq_i$  will be done, but the quantity of heat absorbed will generally not be  $dQ$  but a different quantity, say  $d_1 Q$ .

Write  $2d'Q = +dQ - d_1Q, \dots \dots \dots (1)$

and  $+d^0Q = +dQ - d'Q; \dots \dots \dots (2)$

therefore  $-d^0Q = -d_1Q - d'Q. \dots \dots \dots (3)$

We have  $+dQ = +d^0Q + d'Q, \dots \dots \dots (4)$

and  $-d_1Q = -d^0Q + d'Q; \dots \dots \dots (5)$

thus  $d^0Q$  is the reversible, and  $d'Q$  the irreversible part of the heat absorbed. Now, if we assume that these quantities are of the form

$$d^0Q = \sum R_i^0 dq_i; \quad d'Q = \sum R_i' dq_i, \dots \dots \dots (6)$$

we may consider the new quantities

$$\delta^0Q = \sum R_i^0 \delta q_i; \quad \delta'Q = \sum R_i' \delta q_i, \dots \dots \dots (7)$$

$\delta^0Q + \delta'Q$  gives again  $\delta Q$ . Let us generally define  $\delta Q, \delta^0Q, \delta'Q$  to represent the expressions which result if in the expressions of the quantities  $dQ, d^0Q,$  and  $d'Q$  (which we suppose to be empirically known\*), variations  $\delta q_i$  are substituted in place of the corresponding differentials  $dq_i$ .

§ 2. *Statement of the Principle.*—Let us consider a given period of time, from  $t=t_0$  to  $t=t_1$ . Let  $\delta q_i, \delta s_i, \delta T, \delta U, \sum P_i \delta q_i$ , as usual, represent variations which, between the limits  $t=t_0$  and  $t=t_1$ , are functions of the time susceptible of being differentiated, and which vanish at these limits themselves; finally, let  $\delta Q, \delta^0Q, \delta'Q$  be the corresponding infinitesimal expressions calculated as above stated. The following principle seems then to hold in physical phenomena: between  $t=t_0$  and  $t=t_1$  events which occur in the system must be such that the equation

$$\int_{t_0}^{t_1} dt \{ \delta T - \delta U + \sum P_i \delta q_i + \delta Q \} = 0 \dots \dots (I.)$$

is satisfied. For brevity, this, when necessary, will be referred to as the *Thermokinetic Principle*.

\* To write down the expressions of  $dQ$  and  $d'Q$ , a much greater number of variables would evidently be required in most cases than to write  $d^0Q$ ; thus in most cases many of the coefficients  $R_i^0$  will be equal to zero. A similar remark applies to the coefficients  $P_i, \partial T / \partial q_i, \partial T / \partial s_i,$  and  $\partial U / \partial q_i$ .

§ 3. *Lagrangian Equations.*—From (I.), remembering the definitions laid down, we obtain by a well-known calculation

$$\frac{d}{dt} \left( \frac{\partial T}{\partial s_i} \right) - \frac{\partial T}{\partial q_i} + \frac{\partial U}{\partial q_i} - P_i - R_i = 0. \quad \dots \quad (\text{II.})$$

These equations, a thermokinetic extension of Lagrange's well-known dynamical equations, have been given implicitly by Helmholtz and explicitly by M. Duhem; the form they take in an important particular case had been previously explained by Lord Rayleigh.

§ 4. *Conservation of Energy.*—Considering a real transformation  $dq_i, ds_i$ , multiply each of these equations by  $s_i dt$  respectively, and add; we find

$$dT + dU - \sum P_i dq_i - dQ = 0. \quad \dots \quad (1)$$

The principle of conservation of energy in its general form is thus seen to follow from the thermokinetic principle. That inversely the thermokinetic principle cannot be deduced from conservation of energy is an obvious proposition which scarcely requires special mention.

§ 5. *Free Energy.*—We shall suppose in the following (except when the contrary is expressly stated) that *one* independent variable is the temperature; and accordingly we shall use  $q_i$  to indicate all the *other* variables. That work is not required for merely changing the temperature of a system is an experimental fact; hence, when the variables  $\mathfrak{S}, q_i$ , and  $s_i$  receive increments  $\delta\mathfrak{S}, \delta q_i, \delta s_i$ , the work done on the system will be still  $\sum P_i \delta q_i$  (in our present modified notation) and no term including  $\delta\mathfrak{S}$  will appear. Variables with such properties attributed to them have been employed by Lord Kelvin as long ago as 1855; they have been often adopted in general thermodynamical investigations. M. Duhem calls them "normal" variables.

Let us suppose that  $\mathfrak{S}, q_i$  represent a system of "normal" variables. Write

$$\sum \frac{\partial U}{\partial q_i} \delta q_i - \sum R_i \delta q_i = \sum \frac{\partial V}{\partial q_i} \delta q_i. \quad \dots \quad (1)$$

The function  $V$ , if it exists, will be called *the free energy* of the system, because, as we shall find hereafter,  $V$  defined by equation (1) will agree in the case of Reversible Thermo-

dynamics with what, from Helmholtz, received that designation. Equation (I.) accordingly becomes

$$\int_{t_0}^{t_1} dt \left\{ \delta T - \sum \frac{\partial V}{\partial q_i} \delta q_i + \sum P_i \delta q_i - \left( \frac{\partial U}{\partial \mathfrak{S}} - R_{\mathfrak{S}}^0 \right) \delta \mathfrak{S} + \delta' Q \right\} = 0. \quad (2)$$

Now let us further assume that the following equations are true:—

$$\frac{\partial T}{\partial \mathfrak{S}} = 0; \quad \frac{\partial T}{\partial \frac{d\mathfrak{S}}{dt}} = 0; \quad . . . . . \quad (3)$$

they are found to hold good in all cases of which we have precise knowledge; lastly, let us suppose that there is no term containing  $\delta \mathfrak{S}$  in the expression for  $\delta' Q$ . (With respect to this point compare § 12.) Equation (2) may now be divided into

$$\frac{\partial U}{\partial \mathfrak{S}} - R_{\mathfrak{S}}^0 = 0, \quad . . . . . \quad (4)$$

and

$$\int_{t_0}^{t_1} dt \left\{ \delta T - \sum \frac{\partial V}{\partial q_i} \delta q_i + \sum P_i \delta q_i + \delta' Q \right\} = 0. \quad (III.)$$

This equation expresses the principle in a form similar to that of equation (I.). It is a useful equation, owing to the readiness with which it admits of application in various cases, but its abstract generality is of course much more restricted than that of the fundamental equation.

§ 6. *Reversible Dynamics.*—In Dynamics properly so-called, *i. e.* in Reversible Dynamics, ideal phenomena of motion are dealt with, and the notion of temperature is not taken into account. Therefore, in Reversible Dynamics a function  $V$  can be considered, depending on the remaining variables  $q_i$  only, which does not differ, except by a constant, from the “potential energy”  $U$ ; this is a remark already made by M. Duhem. Of course it must be restricted to the Dynamics of points and of rigid bodies, since, for instance, in Hydrodynamics and Aerodynamics the difference between the quantities  $V$  and  $U$  is variable and depends on the compressibility of the fluid.

From (III.) we obtain, leaving out the irreversible term  $\delta' Q$ , the fundamental principle of Reversible Dynamics.

§ 7. *Electromagnetic irreversible phenomena.*—Energy stored in the æther can be transferred to matter and converted into heat; this phenomenon, when it occurs, is a thoroughly irreversible one.

Here, therefore, we may put  $R_i^0=0$  and  $\partial U/\partial q_i = \partial V/\partial q_i$ ; and the equation will be

$$\int_{t_0}^{t_1} dt \{ \delta T - \delta U + \sum P_i \delta q_i + \delta' Q \} = 0. \quad (1)$$

We shall return to this case in § 13 below.

§ 8. *Reversible Thermodynamics.*—At present the immediate object of the science called Thermodynamics is the study of states of equilibrium. The modifications assumed in Thermodynamics to occur in a system are, for that reason, virtual reversible transformations which lead from one state of equilibrium to another one. Let us admit the following assumptions:—first, that that part of the energy which we call  $T$  is a constant quantity; secondly, that the variables are “normal” variables; thirdly, if a function of the variables  $\mathfrak{S}$  and  $q_i$ , called the entropy, be denoted by  $S$ , that the term  $\delta' Q$  is of the form

$$\mathfrak{S} \frac{\partial S}{\partial \mathfrak{S}} \delta \mathfrak{S} + \mathfrak{S} \sum \frac{\partial S}{\partial q_i} \delta q_i; \quad (1)$$

and, lastly, that the supposed transformation being reversible, the term  $\delta' Q$  is equal to zero. Hence the laws of ordinary Thermodynamics must be contained in

$$\frac{\partial U}{\partial \mathfrak{S}} - \mathfrak{S} \frac{\partial S}{\partial \mathfrak{S}} = 0, \quad (2)$$

and

$$\int_{t_0}^{t_1} dt \left\{ - \sum \frac{\partial V}{\partial q_i} \delta q_i + \sum P_i \delta q_i \right\} = 0, \quad (3)$$

where

$$\frac{\partial V}{\partial q_i} = \frac{\partial U}{\partial q_i} - \mathfrak{S} \frac{\partial S}{\partial q_i}. \quad (4)$$

Since the adopted variables  $\mathfrak{S}$ ,  $q_i$  are “normal” ones, we are at liberty to define the quantity  $U - \mathfrak{S}S$  as representing what in § 5 has been called the *free energy* of the system; hence

$$- \frac{\partial V}{\partial q_i} + P_i = 0; \quad \frac{\partial V}{\partial \mathfrak{S}} + S = 0, \quad (5)$$

and thus we are led to that well-known form of thermodynamical equations which we have learned from MM. Massieu, Gibbs, Duhem, Helmholtz, and others.

§ 9. *Irreversible Dynamics.*—Let us now proceed to consider cases of motion bearing perfect analogy with ordinary

dynamical phenomena, except that, being irreversible, they do not satisfy the condition  $d'Q=0$ . Lord Rayleigh has shown how in many cases we can put

$$d'Q = -2Fdt, \dots \dots \dots (1)$$

employing  $F$  to indicate a function of the variables  $q_i$  (supposed to be "normal" ones) and  $s_i$ , homogeneous of the second degree with respect to the  $s_i$ , which he calls the Dissipation Function. The assumption we make is therefore that

$$d'Q = -dt \sum s_i \frac{\partial F}{\partial s_i} = -\sum \frac{\partial F}{\partial s_i} dq_i; \dots \dots (2)$$

and that

$$R'_i = -\frac{\partial F}{\partial s_i}; \dots \dots \dots (3)$$

following the rule laid down in § 1 we put

$$\delta'Q = -\sum \frac{\partial F}{\partial s_i} \delta q_i, \dots \dots \dots (4)$$

and from (III.) we obtain

$$\int_{t_0}^{t_1} dt \{ \delta T - \sum \frac{\partial V}{\partial q_i} \delta q_i + \sum P_i \delta q_i - \sum \frac{\partial F}{\partial s_i} \delta q_i \} = 0; \dots (5)$$

hence

$$\frac{d}{dt} \left( \frac{\partial T}{\partial s_i} \right) - \frac{\partial T}{\partial q_i} + \frac{\partial V}{\partial q_i} - P_i + \frac{\partial F}{\partial s_i} = 0. \dots (6)$$

These are Lord Rayleigh's equations, with  $V$  written in the place of  $U$ .

§ 10. *Irreversible Hydrodynamics.*—Let us now proceed to consider a viscous fluid; we shall call  $\mu$  its coefficient of viscosity. Owing to the viscosity of the fluid its motion is accompanied by irreversible production of heat; owing to its compressibility, there is reversible production or destruction of heat. We shall suppose that every such loss or gain in every element of the fluid is being immediately and exactly compensated, so that the temperature of the element remains constant. At the interior of a large quantity of fluid we take a portion, of mass  $\iiint dx dy dz \rho$ ,  $\rho$  being the density at the point  $(x, y, z)$ . Let  $p$  be the ordinary mean pressure;  $u, v, w$  the components of the velocity,  $X, Y, Z$  the components of the extraneous acceleration, at the point  $(x, y, z)$  and time  $t$ . The equations of motion, as given by Navier, Poisson, Stokes, and Maxwell, are as follows:—

$$-\rho \frac{du}{dt} + \rho X - \frac{\partial p}{\partial x} + \mu \nabla^2 u + \frac{1}{3} \mu \frac{\partial \theta}{\partial x} = 0, \dots \quad (1)$$

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with the usual signification of  $\nabla^2$  and  $\theta$ . Write

$$p_x dS, \quad p_y dS, \quad p_z dS \quad \dots \quad (2)$$

for the pressures, parallel to the co-ordinate axes, on the element  $dS$  of the boundary of the portion we are considering. If the direction of the inwardly directed normal be denoted by  $n$ , we shall have :—

$$p_x = [p - 2\mu \left( \frac{\partial u}{\partial x} - \frac{1}{3} \theta \right)] \cos(nx) - \mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \cos(ny) \\ - \mu \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \cos(nz); \dots \quad (3)$$

$$p_y = -\mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \cos(nx) + [p - 2\mu \left( \frac{\partial v}{\partial y} - \frac{1}{3} \theta \right)] \cos(ny) \\ - \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \cos(nz); \dots \quad (4)$$

$$p_z = -\mu \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \cos(nx) - \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \cos(ny) \\ + [p - 2\mu \left( \frac{\partial w}{\partial z} - \frac{1}{3} \theta \right)] \cos(nz). \dots \quad (5)$$

If now a system  $\delta x, \delta y, \delta z$  of infinitesimal virtual displacements be imposed upon the fluid, the temperature being kept constant, then the work  $\sum P_i \delta q_i$  done by extraneous forces will be

$$\iint dS (p_x \delta x + p_y \delta y + p_z \delta z) + \iiint dx dy dz \rho (X \delta x + Y \delta y + Z \delta z); \quad (6)$$

the variation of the energy  $T$  will be

$$\delta T = \iiint dx dy dz \rho (u \delta u + v \delta v + w \delta w); \dots \quad (7)$$

the variation of the energy  $V$ , which in Hydrodynamics it is usual\* to call "intrinsic" energy, will be

\* See, for example, that otherwise excellent treatise 'Hydrodynamics' by Prof. Lamb, ed. 1895, pp. 11-12, 469, 507. It is not with the true intrinsic energy  $U$ , but with the *free* energy  $V$  that we are here concerned; the customary use of the word "intrinsic" seems, therefore, to involve a serious error.



$$\delta V = -\iiint dx dy dz p \left( \frac{\partial \delta x}{\partial x} + \frac{\partial \delta y}{\partial y} + \frac{\partial \delta z}{\partial z} \right), \quad \dots \quad (8)$$

and, lastly, the quantity of heat which must be "absorbed" in order to compensate the effects of viscosity will be

$$d'Q = -\iiint dx dy dz 2\mu dt \left\{ \begin{aligned} & \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial z} \right)^2 - \frac{1}{3}\theta^2 \\ & + \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right)^2 + \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)^2 + \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 \end{aligned} \right\}$$

$$= -\iiint dx dy dz 2\mu \left\{ \begin{aligned} & \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right) \frac{\partial dx}{\partial x} + \left( \frac{\partial v}{\partial y} - \frac{1}{3}\theta \right) \frac{\partial dy}{\partial y} + \left( \frac{\partial w}{\partial z} - \frac{1}{3}\theta \right) \frac{\partial dz}{\partial z} \\ & + \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \left( \frac{\partial dz}{\partial y} + \frac{\partial dy}{\partial z} \right) \\ & + \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \left( \frac{\partial dx}{\partial z} + \frac{\partial dz}{\partial x} \right) \\ & + \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \left( \frac{\partial dy}{\partial x} + \frac{\partial dx}{\partial y} \right). \end{aligned} \right\} \quad (9)$$

In order, therefore, to comply with the rule respecting  $\delta'Q$  we have to write

$$\delta'Q = -\iiint dx dy dz 2\mu \left\{ \begin{aligned} & \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right) \frac{\partial \delta x}{\partial x} + \left( \frac{\partial v}{\partial y} - \frac{1}{3}\theta \right) \frac{\partial \delta y}{\partial y} \\ & + \left( \frac{\partial w}{\partial z} - \frac{1}{3}\theta \right) \frac{\partial \delta z}{\partial z} + \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \left( \frac{\partial \delta z}{\partial y} + \frac{\partial \delta y}{\partial z} \right) \\ & + \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \left( \frac{\partial \delta x}{\partial z} + \frac{\partial \delta z}{\partial x} \right) \\ & + \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \left( \frac{\partial \delta y}{\partial x} + \frac{\partial \delta x}{\partial y} \right). \end{aligned} \right\} \quad (10)$$

Let us now verify whether in the present case our general principle applies. From (1) we find

$$\int_{t_0}^{t_1} dt \iiint dx dy dz \left\{ \begin{aligned} & \left[ -\rho \frac{du}{dt} + \rho X - \frac{\partial p}{\partial x} + \mu \nabla^2 u + \frac{1}{3}\mu \frac{\partial \theta}{\partial x} \right] \delta x \\ & + [\dots] \delta y + [\dots] \delta z \end{aligned} \right\} = 0; \quad (11)$$

now

$$\nabla^2 u + \frac{1}{3} \frac{\partial \theta}{\partial x} = 2 \frac{\partial}{\partial x} \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right) + \frac{\partial}{\partial z} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right), \quad \dots \quad (12)$$

so that from (8), (10), (12), and again from (3), (4), (5) we obtain

$$\begin{aligned}
 & \iiint dx dy dz \left\{ \left[ -\frac{\partial p}{\partial x} + \mu \nabla^2 u + \frac{1}{3} \mu \frac{\partial \theta}{\partial x} \right] \delta x + [\dots] \delta y + [\dots] \delta z \right\} \\
 & = -\delta V + \delta' Q - \iiint dx dy dz \left\{ \frac{\partial}{\partial x} (p \delta x) + \frac{\partial}{\partial y} (p \delta y) + \frac{\partial}{\partial z} (p \delta z) \right\} \\
 & + \iiint dx dy dz 2\mu \left\{ \frac{\partial}{\partial x} \left[ \left( \frac{\partial u}{\partial x} - \frac{1}{3} \theta \right) \delta x \right] + \frac{\partial}{\partial y} \left[ \left( \frac{\partial v}{\partial y} - \frac{1}{3} \theta \right) \delta y \right] + \frac{\partial}{\partial z} \left[ \left( \frac{\partial w}{\partial z} - \frac{1}{3} \theta \right) \delta z \right] \right\} \\
 & + \iiint dx dy dz \mu \left\{ \begin{array}{l} \frac{\partial}{\partial y} \left[ \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \delta z \right] + \frac{\partial}{\partial z} \left[ \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \delta y \right] + \\ \frac{\partial}{\partial z} \left[ \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \delta x \right] + \frac{\partial}{\partial x} \left[ \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \delta z \right] + \\ \frac{\partial}{\partial x} \left[ \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \delta y \right] + \frac{\partial}{\partial y} \left[ \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \delta x \right] \end{array} \right\} \\
 & = -\delta V + \delta' Q + \iint dS (p_x \delta x + p_y \delta y + p_z \delta z) \dots \dots \dots (13)
 \end{aligned}$$

Further, we see that

$$- \int_{t_0}^t dt \iiint dx dy dz \rho \left( \frac{du}{dt} \delta x + \frac{dv}{dt} \delta y + \frac{dw}{dt} \delta z \right) = \int_{t_0}^t dt \delta T, \quad (14)$$

because  $dx dy dz \rho$  does not vary; and collecting our results we see that (11) reduces to

$$\int_{t_0}^t dt \{ \delta T - \delta V + \sum P_i \delta q_i + \delta' Q \} = 0, \dots \dots (14)$$

with equations (7), (8), (6), (10) to define the terms within brackets.

§ 11. *Diffusion*. — We next take two gases which are diffusing into one another. Let the masses of the portions considered be  $\iiint dx_1 dy_1 dz_1 \rho_1$  and  $\iiint dx_2 dy_2 dz_2 \rho_2$ ; and  $S_1$  and  $S_2$  their respective boundaries. When the motion of the gases is going on, three irreversible phenomena will occur, viz., internal friction in the first gas, internal friction in the second, and mutual interdiffusion of both; in the following both the first and the second are neglected. Let again  $u_1, v_1, w_1, u_2, v_2, w_2$  denote the velocity components,  $X_1, Y_1, Z_1, X_2, Y_2, Z_2$  those of extraneous acceleration,  $p_1, p_2$  the mean pressure, at the time  $t$  and a given point of space, where at that time both the elements  $dx_1 dy_1 dz_1$  and  $dx_2 dy_2 dz_2$  of the gases happen to be momentarily situated. The quantities  $u_1$  and  $u_2, v_1$  and  $v_2,$

$w_1$  and  $w_2$  being, however, quite different, the elements will, of course, separate after a time infinitely short; likewise  $\delta x_1$  and  $\delta x_2$ ,  $\delta y_1$  and  $\delta y_2$ ,  $\delta z_1$  and  $\delta z_2$  must be understood to be quite independent variations. Let us write

$$\int_{t_0}^{t_1} dt \{ \delta T - \delta V + \Sigma P_i \delta q_i + \delta' Q \} = 0, \dots (1)$$

and let us adopt, as a definition of the terms, the following equations:—

$$\delta T = \delta T_1 + \delta T_2, \dots (2)$$

$$\delta V = \delta V_1 + \delta V_2, \dots (3)$$

$$T_1 = \frac{1}{2} \iiint dx_1 dy_1 dz_1 \rho_1 (u_1^2 + v_1^2 + w_1^2), \dots (4)$$

$$T_2 = \frac{1}{2} \iiint dx_2 dy_2 dz_2 \rho_2 (u_2^2 + v_2^2 + w_2^2), \dots (5)$$

$$\delta V_1 = - \iiint dx_1 dy_1 dz_1 p_1 \left( \frac{\partial \delta x_1}{\partial x_1} + \frac{\partial \delta y_1}{\partial y_1} + \frac{\partial \delta z_1}{\partial z_1} \right), \dots (6)$$

$$\delta V_2 = - \iiint dx_2 dy_2 dz_2 p_2 \left( \frac{\partial \delta x_2}{\partial x_2} + \frac{\partial \delta y_2}{\partial y_2} + \frac{\partial \delta z_2}{\partial z_2} \right), \dots (7)$$

$$\begin{aligned} \Sigma P_i \delta q_i = & \iiint dx_1 dy_1 dz_1 \rho_1 (X_1 \delta x_1 + Y_1 \delta y_1 + Z_1 \delta z_1) \\ & + \iiint dx_2 dy_2 dz_2 \rho_2 (X_2 \delta x_2 + Y_2 \delta y_2 + Z_2 \delta z_2) \\ & + \iiint dS_1 p_1 \{ \cos(n_1 x) \delta x_1 + \cos(n_1 y) \delta y_1 + \cos(n_1 z) \delta z_1 \} \\ & + \iiint dS_2 p_2 \{ \cos(n_2 x) \delta x_2 + \cos(n_2 y) \delta y_2 + \cos(n_2 z) \delta z_2 \}. \end{aligned} \quad (8)$$

The quantity of heat generated in time  $dt$  by diffusion may be written

$$\iiint dx dy dz \Lambda \rho_1 \rho_2 \{ (u_2 - u_1)(dx_2 - dx_1) + (v_2 - v_1)(dy_2 - dy_1) + (w_2 - w_1)(dz_2 - dz_1) \}, \quad (9)$$

the expression  $dx dy dz$  being understood to mean indifferently  $dx_1 dy_1 dz_1$  or  $dx_2 dy_2 dz_2$ , and  $\Lambda$  being a constant coefficient intimately connected with the "coefficient of diffusion" of the gases. If the temperature is to remain constant, the quantity (9) must be taken away; hence

$$\begin{aligned} \delta' Q = & - \iiint dx dy dz \Lambda \rho_1 \rho_2 \{ (u_2 - u_1)(\delta x_2 - \delta x_1) \\ & + (v_2 - v_1)(\delta y_2 - \delta y_1) + (w_2 - w_1)(\delta z_2 - \delta z_1) \}. \end{aligned} \quad (10)$$

Substituting (2), (3), . . . . (8), and (10) in (1), we find

$$\int_{t_0}^{t_1} dt \iiint dx dy dz \left\{ \begin{aligned} & \left[ -\rho_1 \frac{du_1}{dt} - \frac{\partial p_1}{\partial x_1} + \rho_1 X_1 + A\rho_1\rho_2(u_2 - u_1) \right] \delta x_1 \\ & \qquad \qquad \qquad + [\dots] \delta y_1 + [\dots] \delta z_1 \\ & + \left[ -\rho_2 \frac{du_2}{dt} - \frac{\partial p_2}{\partial x_2} + \rho_2 X_2 + A\rho_2\rho_1(u_1 - u_2) \right] \delta x_2 \\ & \qquad \qquad \qquad + [\dots] \delta y_2 + [\dots] \delta z_2 \end{aligned} \right\} = 0, \quad (11)$$

which shows at once that

$$\rho_1 \frac{du_1}{dt} + \frac{\partial p_1}{\partial x_1} = \rho_1 X_1 + A\rho_1\rho_2(u_2 - u_1), \text{ \&c.} \quad (12)$$

$$\rho_2 \frac{du_2}{dt} + \frac{\partial p_2}{\partial x_2} = \rho_2 X_2 + A\rho_2\rho_1(u_1 - u_2), \text{ \&c.} \quad (13)$$

These equations have been established long ago by Maxwell and Stefan.

§ 12. *Conduction of Heat.*—Fourier’s equation of conduction of heat appears to belong to the class of conservation of energy equations. At first let us avoid employing “normal” variables. Since the motion of the medium and the intervention of extraneous forces are immaterial for conduction of heat, we may put  $\delta T = 0$ ,  $\sum P_i \delta q_i = 0$ , and  $d^o Q = 0$ ; therefore  $\delta U = \delta V$ , and

$$\int_{t_0}^{t_1} dt \{ -\delta U + \delta' Q \} = 0, \dots \dots \dots (1)$$

or

$$-\frac{\partial U}{\partial q_i} + R'_i = 0. \dots \dots \dots (2)$$

Hence, in any real transformation, we have

$$-\frac{dU}{dt} + \frac{d'Q}{dt} = 0, \dots \dots \dots (3)$$

that is to say, in “normal” variables :—

$$\frac{\partial U}{\partial \vartheta} \frac{d\vartheta}{dt} = -\sum \frac{\partial U}{\partial q_i} \frac{dq_i}{dt} + \frac{d'Q}{dt} \dots \dots \dots (4)$$

This is the general form of Fourier’s equation; usually  $\partial U / \partial \vartheta$  is assumed to be of the form  $dx dy dz \rho c_v$  in an element  $dx dy dz$ ,  $\rho$  being the density and  $c_v$  the well-known thermal capacity; and the remaining  $\partial U / \partial q_i$  are usually neglected. We shall reconsider the present case from a different standpoint in § 19.

§ 13. *Electromagnetic Dissipation.* — In Helmholtz's memoir "Das Princip der kleinsten Wirkung in der Elektrodynamik" \*, it is shown in great generality that the thermokinetic principle holds for electromagnetic phenomena; nevertheless we beg leave to consider here the simplest (but for our purpose most important) case, to which in the second part of the paper we shall have again to refer. Consider isotropic conducting substances, at rest. Let us suppose that energy-dissipation of the simplest or Joulean type is the only possible irreversible phenomenon. Let the components of electromotive intensity at the point  $(x, y, z)$  be  $E_x, E_y, E_z$ ; those of extraneous electric forces,  $F_x, F_y, F_z$ ; and the components of magnetic force  $H_x, H_y, H_z$ . Let  $C$  be the electric conductivity,  $K$  the dielectric inductive capacity, and  $\mu$  the magnetic permeability. If

$$E_x = -\frac{dA_x}{dt}, \quad E_y = -\frac{dA_y}{dt}, \quad E_z = -\frac{dA_z}{dt}, \quad \dots \quad (1)$$

then the vector  $A$ , whose components  $A_x, A_y, A_z$  are, may be taken to represent the "electromagnetic momentum" at  $(x, y, z)$ . We assume that

$$\left. \begin{aligned} 4\pi C(E_x - F_x) + K \frac{dE_x}{dt} &= \frac{\partial H_x}{\partial y} - \frac{\partial H_y}{\partial z}, \\ 4\pi C(E_y - F_y) + K \frac{dE_y}{dt} &= \frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x}, \\ 4\pi C(E_z - F_z) + K \frac{dE_z}{dt} &= \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y}; \end{aligned} \right\} \dots \quad (2)$$

$$\left. \begin{aligned} \mu H_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}, \\ \mu H_y &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}, \\ \mu H_z &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}; \end{aligned} \right\} \dots \quad (3)$$

Mr. Heaviside and H. Hertz, it is well known, have constructed the whole of Maxwell's Theory upon two systems of equations, one of which is the system (2) above, whilst the second follows at once from (1) and (3). We shall take  $A_x, A_y, A_z$  to be the independent variables; that is the choice

\* *Sitz. Berl. Akad.* 12 Mai 1892; *Wiss. Abh.* Bd. iii. p. 476. See also Boltzmann, *Vorlesungen über Maxwell's Theorie*, vol. ii. p. 7.

which Lord Kelvin, Prof. Boltzmann, and other writers adopted when endeavouring to find dynamical analogies for electromagnetic phenomena. The part of the energy, called T, which depends on the quantities  $dA_x/dt$ ,  $dA_y/dt$ ,  $dA_z/dt$ , will be then the electric energy

$$T = \frac{1}{8\pi} \iiint dx dy dz K(E_x^2 + E_y^2 + E_z^2); \quad \dots (4)$$

the other U, connected with the collocation of the variables  $A_x$ ,  $A_y$ ,  $A_z$  themselves, will be

$$U = \frac{1}{8\pi} \iiint dx dy dz \mu(H_x^2 + H_y^2 + H_z^2). \quad \dots (5)$$

Supposing  $\delta A_x$ ,  $\delta A_y$ ,  $\delta A_z$  to be variations as usual and K, C,  $\mu$  and  $dx dy dz$  not to be subject to variation, we shall have

$$\frac{1}{4\pi} \int_{t_0}^{t_1} dt \iiint dx dy dz \left\{ \left[ K \frac{dE_x}{dt} - \left( \frac{\partial H_x}{\partial y} - \frac{\partial H_y}{\partial z} \right) - 4\pi C F_x + 4\pi C E_x \right] \delta A_x + [\dots] \delta A_y + [\dots] \delta A_z \right\} = 0. \quad (6)$$

This equation is readily transformed. First :

$$\frac{1}{4\pi} \int_{t_0}^{t_1} dt \iiint dx dy dz K \left( \frac{dE_x}{dt} \delta A_x + \frac{dE_y}{dt} \delta A_y + \frac{dE_z}{dt} \delta A_z \right) = \int_{t_0}^{t_1} dt \delta T, \quad (7)$$

and

$$- \int_{t_0}^{t_1} dt \iiint dx dy dz C (F_x \delta A_x + F_y \delta A_y + F_z \delta A_z) = \int_{t_0}^{t_1} dt \Sigma P_i \delta q_i. \quad (8)$$

Then, from the well-known Maxwell-Helmholtz principle, on the continuity of properties on surfaces of separation between different media, and from the equations (3), we obtain

$$\begin{aligned} & - \frac{1}{4\pi} \int_{t_0}^{t_1} dt \iiint dx dy dz \left\{ \left( \frac{\partial H_x}{\partial y} - \frac{\partial H_y}{\partial z} \right) \delta A_x + \left( \frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} \right) \delta A_y \right. \\ & \qquad \qquad \qquad \left. + \left( \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} \right) \delta A_z \right\} \\ & = \frac{1}{4\pi} \int_{t_0}^{t_1} dt \iiint dx dy dz \frac{1}{\mu} \left\{ \begin{aligned} & \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \frac{\partial \delta A_x}{\partial y} - \left( \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \frac{\partial \delta A_x}{\partial z} \\ & + \left( \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) \frac{\partial \delta A_y}{\partial z} - \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \frac{\partial \delta A_y}{\partial x} \\ & + \left( \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \frac{\partial \delta A_z}{\partial x} - \left( \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) \frac{\partial \delta A_z}{\partial y} \end{aligned} \right\} \\ & = - \int_{t_0}^{t_1} dt \delta U. \quad \dots \dots \dots (9) \end{aligned}$$

If, therefore, the general principle is applicable here, the terms in (6) containing  $4\pi CE_x$ , &c., should reduce to

$$+ \int_{t_0}^{t_1} dt \delta'Q. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Now the quantity of energy which becomes absorbed from the æther and converted into heat is, for the time  $dt$  and the volume  $\iiint dx dy dz$ ,

$$- \iiint dx dy dz C(E_x dA_x + E_y dA_y + E_z dA_z); \quad . \quad (11)$$

hence

$$\delta'Q = \iiint dx dy dz C(E_x \delta A_x + E_y \delta A_y + E_z \delta A_z); \quad . \quad (12)$$

and thus the principle contained in (I.), or in (III.), is again seen to hold good.

## PART II.

§ 14. *Introductory.*—The foregoing naturally raises the question, Does a *general* law exist concerning the infinitesimal expressions  $d'Q$  and  $\delta'Q$ , which have been found to characterize dissipation of energy in the various particular cases discussed? I venture to answer this in the affirmative; but the hypothesis I advance does not profess to be more than a conjecture and an approximation.

Let us consider in every particular case the quantity

$$\frac{d'Q}{dt} = -2F \text{ say.} \quad . \quad . \quad . \quad . \quad . \quad (IV.)$$

In the case of irreversible Dynamics, § 9, the function  $F$  is well known, and has been called by Lord Rayleigh the "Dissipation Function;" I should suggest that this term be extended to all cases covered by equation (IV.).

Let us imagine a material (or at any rate partly material) system. Suppose that it is *not* in equilibrium, and observe, in a quantitative manner, the disturbances which its state involves. Let it be isolated so as not to be disturbed by extraneous action. We know from experience that under such circumstances the disturbances in the system must finally subside and tend to disappear. This general behaviour may be called *the coercion* of disturbances, because of the contrast it offers with inertia. (See *Phil. Mag.* for June 1895, p. 509.) For definiteness let us consider a continuous body. Let  $dx dy dz \rho$  be the mass of an element  $dx dy dz$ , and let  $dx dy dz \rho f$  represent its dissipation function, so that  $F$ , the dissipation function for the portion  $\iiint dx dy dz$  of the body,

be  $= \iiint dx dy dz \rho f$ . Then, generally speaking,  $F$  is susceptible of three kinds of variation, and  $dF/dt$  is the sum of three terms:—1. A surface-integral relating to the action between the body and the exterior world through the boundary of the body; 2. A volume-integral expressing “action at a distance” between the body and the exterior world; and 3. A volume-integral representing “coercion,” *i. e.*, that intimate action whose constant tendency it is to attenuate and finally to efface inequalities and disturbances, if there is no extraneous action to maintain or to excite them; and whose ultimate nature is, of course, unknown to us. It would not be difficult to translate our statement into symbols. Let us adopt, for instance, that general Molecular Theory due to Maxwell, which we have called (on a former occasion) “Kinematical Molecular Theory.” Let  $u + \xi$ ,  $v + \eta$ ,  $w + \zeta$  denote the components of the velocities of individual molecules,  $f$  a function of the  $(u + \xi)$ ,  $(v + \eta)$ , and  $(w + \zeta)$ ,  $\bar{f}$  the mean value of  $f$  within an element, and  $D/Dt$  the rate of “coercion.” Then

$$\rho \frac{d\bar{f}}{dt} = - \left\{ \frac{\partial}{\partial x} (\rho \bar{\xi} f) + \frac{\partial}{\partial y} (\rho \bar{\eta} f) + \frac{\partial}{\partial z} (\rho \bar{\zeta} f) \right\} + \rho \left( X \frac{\partial \bar{f}}{\partial u} + Y \frac{\partial \bar{f}}{\partial v} + Z \frac{\partial \bar{f}}{\partial w} \right) + \rho \frac{D\bar{f}}{Dt}, \dots (1)$$

hence

$$\begin{aligned} \frac{dF}{dt} &= \frac{d}{dt} \iiint dx dy dz \rho \bar{f} \\ &= \iiint dS \rho \{ \bar{\xi} f \cos (nx) + \bar{\eta} f \cos (ny) + \bar{\zeta} f \cos (nz) \} \\ &+ \iiint dx dy dz \rho \left( X \frac{\partial \bar{f}}{\partial u} + Y \frac{\partial \bar{f}}{\partial v} + Z \frac{\partial \bar{f}}{\partial w} \right) + \iiint dx dy dz \rho \frac{D\bar{f}}{Dt}. \end{aligned} (2)$$

The three terms on the right-hand side refer to the three kinds of variation as above stated.

The assumption we propose to examine is that the third, or coercive term  $DF/Dt$  is always proportional to the value of  $F$ . Thus, writing  $\tau$  for a constant period of time,

$$\frac{DF}{Dt} = - \frac{2F}{\tau} \dots \dots \dots (V.)$$

This equation, we shall find, is general; in the neighbourhood of states of equilibrium at least it is exactly fulfilled. The period of time  $\tau$  was first considered by Clerk-Maxwell;



in an important case it received the name of *the modulus of the time of relaxation*\* and may, without inconvenience, be called so in other similar cases.

Equation (V.) may be verified in various cases, which we shall take in order.

§ 15. *Irreversible Hydrodynamics.*—From § 10 we have

$$F = \iiint dx dy dz \mu \left\{ \begin{aligned} & \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right)^2 + \left( \frac{\partial v}{\partial y} - \frac{1}{3}\theta \right)^2 + \left( \frac{\partial w}{\partial z} - \frac{1}{3}\theta \right)^2 \\ & + \frac{1}{2} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right)^2 + \frac{1}{2} \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)^2 + \frac{1}{2} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 \end{aligned} \right\}. \quad (1)$$

Writing  $p_{xx}, \dots, p_{xy}$  for the usual components, we have

$$p_{xx} - p = -2\mu \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right); \quad p_{yz} = -\mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \quad (2)$$

and four other equations of the same form. These equations, it is well known, must be fulfilled if the dynamical equations of Navier, Poisson, Stokes, and Maxwell are to be true; they may be described, therefore, as being in agreement with experience, and so also may be equation (1). Hence

$$F = \iiint dx dy dz \frac{1}{4\mu} \left\{ \begin{aligned} & (p_{xx} - p)^2 + (p_{yy} - p)^2 + (p_{zz} - p)^2 \\ & + 2p_{yz}^2 + 2p_{zx}^2 + 2p_{xy}^2 \end{aligned} \right\}. \quad (3)$$

Again, if the disturbance is not a very violent one, we have the equations †

$$\frac{D(p_{xx} - p)}{Dt} = 2p \left( \frac{\partial u}{\partial x} - \frac{1}{3}\theta \right); \quad \frac{Dp_{yz}}{Dt} = p \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \quad (4)$$

and four other equations, to be written down from symmetry; it may be well to point out that they are “kinematical” equations, therefore independent of any particular molecular hypothesis. Now, if we put

$$\frac{\mu}{p} = \tau, \quad \dots \dots \dots (5)$$

we obtain from (2) and (4)

$$\frac{D(p_{xx} - p)}{Dt} = -\frac{p_{xx} - p}{\tau}; \quad \frac{Dp_{yz}}{Dt} = -\frac{p_{yz}}{\tau}, \quad \dots \dots (6)$$

\* Philosophical Transactions, 1867, p. 82. See also ‘Treatise on Electricity and Magnetism,’ third edition, vol. i. p. 451.

† Philosophical Transactions, 1867, p. 81.

and four similar equations ; and from (3) and (6)

$$F = -\iiint dx dy dz \frac{\tau}{4\mu} \left\{ \begin{aligned} &(p_{xx} - p) \frac{D(p_{xx} - p)}{Dt} + (p_{yy} - p) \frac{D(p_{yy} - p)}{Dt} \\ &+ (p_{zz} - p) \frac{D(p_{zz} - p)}{Dt} \\ &+ 2p_{yz} \frac{Dp_{yz}}{Dt} + 2p_{zx} \frac{Dp_{zx}}{Dt} + 2p_{xy} \frac{Dp_{xy}}{Dt} \end{aligned} \right\}, \quad (7)$$

whence, by (3), we infer that  $DF/Dt = -2F/\tau$ , as stated above.

The value of  $\tau$  in air, at the temperature  $0^\circ$  C. and normal pressure, is approximately  $2.10^{-10}$  of a second (Maxwell, Phil. Trans. 1867, p. 83). We may also compare the relative values of  $\tau$  in two fluids. In doing so we may assume, in accordance with Prof. Van der Waals' leading idea, that the values of  $\tau$  would bear a constant proportion if they were calculated for "corresponding" states of the fluids\*. Hence the coefficients of viscosity will likewise, in corresponding states of two fluids, bear a constant numerical ratio †.

§ 16. *Diffusion*.—The signification of the symbols being the same as in § 11, we find the dissipation function of diffusion to be

$$F = \frac{1}{2} \iiint dx dy dz A\rho_1\rho_2 \{ (u_2 - u_1)^2 + (v_2 - v_1)^2 + (w_2 - w_1)^2 \}. \quad (1)$$

The theory of diffusion can be deduced, in the case of two gases, from "kinematical" equations and from the following equations "of coercion," in which  $D/Dt$  refers to the total coercive action of both gases :

$$\frac{Du_1}{Dt} = A\rho_2(u_2 - u_1) ; \quad \frac{Du_2}{Dt} = A\rho_1(u_1 - u_2), \quad . \quad (2)$$

and four other equations of similar form. If the dynamical equations of Maxwell and Stefan are true, equations (2) must likewise be fulfilled ; they may be said therefore to agree with experience. Let us now pass to the usual case of slow and quiet diffusion (Maxwell, Phil. Trans. 1867, pp. 73-74). If we write  $\mathfrak{S}$  for the temperature,  $R$  for the gaseous constant, we shall find the value of the coefficient of diffusion, or  $h$  say, to be  $R\mathfrak{S}/A(\rho_1 + \rho_2)$  ; and, if  $p = p_1 + p_2$ , the charac-

\* See Kamerlingh Onnes, *Algemeene Theorie der Vloeistoffen*, Tweede Stuk, p. 8, 1881.

† See Kamerlingh Onnes, 'Communications from the Laboratory of Physics at the University of Leiden,' no. 12, p. 11, 1894.

teristic period  $\tau$  for the coercion of the disturbance will be

$$\tau = \frac{1}{A(\rho_1 + \rho_2)} = \frac{(\rho_1 + \rho_2)h}{p} \dots \dots \dots (3)$$

In a system composed of nitrogen and oxygen, at 0° C. and normal pressure, the value of  $\tau$  (from v. Obermayer's experimental results) is about  $4.5 \times 10^{-10}$  of a second. Returning to (2) we obtain

$$\frac{D(u_2 - u_1)}{Dt} = -\frac{u_2 - u_1}{\tau}, \dots \dots \dots (4)$$

and two other equations which may be written down from symmetry; hence (1) reduces to

$$F = -\frac{1}{2} \iiint dx dy dz A \rho_1 \rho_2 \tau \left\{ (u_2 - u_1) \frac{D(u_2 - u_1)}{Dt} + (v_2 - v_1) \frac{D(v_2 - v_1)}{Dt} + (w_2 - w_1) \frac{D(w_2 - w_1)}{Dt} \right\}, \dots \dots (5)$$

and this gives

$$\frac{DF}{Dt} = -\frac{2F}{\tau} \dots \dots \dots (6)$$

Let us verify that, as stated above,  $2F$  is the rate at which, owing to diffusion, heat is being irreversibly generated. First, from conservation of energy, we have

$$\frac{D}{Dt} \iiint dx dy dz \frac{1}{2} \left\{ \rho_1 (u_1^2 + v_1^2 + w_1^2 + \bar{\xi}_1^2 + \bar{\eta}_1^2 + \bar{\zeta}_1^2) + \rho_2 (u_2^2 + v_2^2 + w_2^2 + \bar{\xi}_2^2 + \bar{\eta}_2^2 + \bar{\zeta}_2^2) \right\} = 0. \quad (7)$$

Then, from (2) we obtain

$$\frac{D}{Dt} \iiint dx dy dz \frac{1}{2} \rho_1 (u_1^2 + v_1^2 + w_1^2) = \iiint dx dy dz A \rho_1 \rho_2 \times \{u_1(u_2 - u_1) + v_1(v_2 - v_1) + w_1(w_2 - w_1)\}, \dots (8)$$

$$\frac{D}{Dt} \iiint dx dy dz \frac{1}{2} \rho_2 (u_2^2 + v_2^2 + w_2^2) = \iiint dx dy dz A \rho_2 \rho_1 \times \{u_2(u_1 - u_2) + v_2(v_1 - v_2) + w_2(w_1 - w_2)\}, \dots (9)$$

whence by (7) it follows:—

$$\begin{aligned} & \frac{D}{Dt} \iiint dx dy dz \frac{1}{2} \{ \rho_1 (\bar{\xi}_1^2 + \bar{\eta}_1^2 + \bar{\zeta}_1^2) + \rho_2 (\bar{\xi}_2^2 + \bar{\eta}_2^2 + \bar{\zeta}_2^2) \} \\ & = \iiint dx dy dz A \rho_1 \rho_2 \{ (u_2 - u_1)^2 + (v_2 - v_1)^2 + (w_2 - w_1)^2 \} \\ & = 2F \dots \dots \dots (10) \end{aligned}$$

and this proves the proposition.

§17. *Electromagnetic Dissipation.*—The electromagnetic dissipation function is

$$F = \frac{1}{2} \iiint dx dy dz C(E_x^2 + E_y^2 + E_z^2), \dots (1)$$

the symbols being defined as in § 13. The disturbance settles down obeying the well-known equations

$$K \frac{DE_x}{Dt} = -4\pi CE_x; \quad K \frac{DE_y}{Dt} = -4\pi CE_y; \quad K \frac{DE_z}{Dt} = -4\pi CE_z; \quad (2)$$

they are therefore the electromagnetic “coercion” equations. If we take  $\tau = K/4\pi C$ , as has been done by Maxwell and many others, we see that

$$F = -\frac{1}{2} \iiint dx dy dz \tau C \left( E_x \frac{DE_x}{Dt} + E_y \frac{DE_y}{Dt} + E_z \frac{DE_z}{Dt} \right), \dots (3)$$

and

$$\frac{DF}{Dt} = -\frac{2F}{\tau} \dots (4)$$

Prof. J. J. Thomson has shown\* that for water with 8.3 per cent. of  $H_2SO_4$ ,  $\tau$  cannot differ much from  $2.10^{-11}$  of a second; and for glass at  $200^\circ C$ . from about  $10^{-5}$  of a second.

§ 18. *Irreversible Dynamics.*—In the case of § 17 the energy we have called  $T$  is proportional to the dissipation function  $F$ ; the same holds in § 16 if we have  $\rho_1 u_1 + \rho_2 u_2 = 0$  (see Maxwell, Phil. Trans. 1867, pp. 73-74). Hence, in such cases equation (V.) becomes  $DT/Dt = -2T/\tau$ . Again, in the Irreversible Dynamics of § 9, if the additional dissipative forces  $-R'_i$  be proportional to the corresponding components of momentum, the same proportionality holds. For example, let

$$-R'_i = \frac{1}{\tau} \frac{\partial T}{\partial s_i} \dots (1)$$

represent the additional dissipative force acting in the  $q_i$ -direction; then  $T = \tau F$ ; and since from (5), § 9, it is easily shown that

$$\frac{DT}{Dt} = -2F, \dots (2)$$

\* ‘Notes on Recent Researches in Electricity and Magnetism,’ 1893, § 32.

$D/Dt$  being the rate of variation of the kinetic energy arising from the dissipative forces, we see that, in this case,

$$DF/Dt = -2F/\tau \quad \text{and} \quad DT/Dt = -2T/\tau. \quad (3)$$

*Cf.* Lord Rayleigh, 'The Theory of Sound,' vol. i. p. 78.

§ 19. *Dissipation Function of Conduction.*—In the Philosophical Magazine for June 1895, p. 506, it was shown that in conduction of heat the dissipation function is of the form

$$2F = -\frac{5}{2} \iiint dx dy dz \left\{ \rho r_x \frac{\partial \theta}{\partial x} + \rho r_y \frac{\partial \theta}{\partial y} + \rho r_z \frac{\partial \theta}{\partial z} \right\}, \quad (1)$$

the symbol  $\theta$  being employed to denote  $\frac{1}{3}(\xi^2 + \eta^2 + \zeta^2)$ . From (12) and (39) in the paper referred to, we have

$$\frac{D\rho r_x}{Dt} = 5p_{xx} \frac{\partial \theta}{\partial x}; \quad \frac{D\rho r_y}{Dt} = 5p_{yy} \frac{\partial \theta}{\partial y}; \quad \frac{D\rho r_z}{Dt} = 5p_{zz} \frac{\partial \theta}{\partial z}; \quad (2)$$

$$\frac{D\rho r_x}{Dt} = -\frac{5p_{xx}}{k} \rho r_x; \quad \frac{D\rho r_y}{Dt} = -\frac{5p_{yy}}{k} \rho r_y; \quad \frac{D\rho r_z}{Dt} = -\frac{5p_{zz}}{k} \rho r_z; \quad (3)$$

equations (2) are the "kinematical," and equations (3) the "coercive" equations of the problem. They must be fulfilled in order to make the equations hold :

$$\rho r_x = -k \frac{\partial \theta}{\partial x}, \quad \rho r_y = -k \frac{\partial \theta}{\partial y}, \quad \rho r_z = -k \frac{\partial \theta}{\partial z}, \quad \dots \quad (4)$$

and, therefore, to secure applicability for Fourier's equation. The time of relaxation we define as

$$\tau = k/5p, \quad \dots \dots \dots (5)$$

neglecting differences  $p - p_{xx}$ , &c. From (1) and (4) we obtain

$$2F = \frac{5}{2} \iiint dx dy dz \frac{1}{k} \{ (\rho r_x)^2 + (\rho r_y)^2 + (\rho r_z)^2 \}, \quad (6)$$

and from (1) and (2) we have :

$$2F = -\frac{D}{Dt} \iiint dx dy dz \frac{1}{4p} \{ (\rho r_x)^2 + (\rho r_y)^2 + (\rho r_z)^2 \}, \quad (7)$$

whence, by (5), we find again

$$\frac{DF}{Dt} = -\frac{2F}{\tau} \dots \dots \dots (8)$$

§ 20. *Connexion between the periods  $\tau$ .*—Let  $\tau_F$  be the

characteristic period  $\tau$  for conduction of heat in a given gas, and let  $\tau_M$  denote the period relating, for the same gas, to internal friction. The coefficient of conductivity in Fourier's equation, as usually written, is  $\frac{1}{3}c_p k$ ,  $k$  denoting the same quantity as in § 19. Now in the Kinetic Theory of Gases it is shown that this coefficient is equal to

$$\frac{15}{4}(\gamma-1)c_v\mu, \quad . . . . . (1)$$

if  $\gamma$  be written for the ratio  $c_p/c_v$  of specific heats, and  $\mu$  for the coefficient of viscosity [for example, see Prof. Boltzmann's *Vorlesungen über Gastheorie*, equations (238), (54), and (57)]. Hence

$$\tau_F = \frac{9}{4}(\gamma-1)\tau_M \quad \text{or} \quad = \frac{3}{2}\tau_M, \quad . . . (2)$$

since, strictly speaking, our calculation requires the gas to be monatomic. In a similar manner may all the periods of relaxation, corresponding to the various powers of coercion of a given body, be mutually connected; and every such simple equation, if it holds, is equivalent to a definite physical law.

