CHAPTER XVII

REDUCTION OF THE PRINCIPLES OF THERMODYNAMICS TO THE GENERAL PRINCIPLES OF MECHANICS

Translated by D. H. Delphenich

_____

309. Diverse theories. – The reduction of the principle of equivalence to the fundamental principles of mechanics encounters no difficulties: As we have seen, the hypothesis of molecular forces suffices for one to deduce the principle of the conservation of energy, and consequently, that of the equivalence of the general equations of motion.

Things are different for the second principle of thermodynamics. Clausius was the first to attempt to reduce it to the principles of mechanics, but without success.

Helmholtz, developed a theory that was closer to perfect than that of Clausius in his paper on the *least-action principle*; nevertheless, he accounted for only irreversible phenomena.

310. Foundations of Helmholtz's theory. – Consider a system of material points that are either free or subject to constraints, and whose situation is finite for the parameters q_1, q_2, q_3, …, q_n . Let q'_1, q'_2, …, q'_n denote the derivatives of these parameters with respect to time, and let T denote one-half the *vis viva* of the system. Finally, let:

$$Q_1 \, \delta q_1 + Q_2 \, \delta q_2 + \dots + Q_n \, \delta q_n$$

be the expression for the work that is done by the forces to which the system is subjected under a virtual displacement. At each instant, we will have:

$$\frac{d}{dt}\frac{dT}{dq'_i} - \frac{dT}{dq_i} = 0$$

for each parameter; this is the Lagrange equation for the parameter q_i .

In his paper, Helmholtz routinely changed these notations. The letter T is preserved in order to denote the absolute temperature; the semi-*vis viva* is then represented by L. The parameters are called p_a, p_b, …, and their derivatives with respect to time are represented by q_a, q_b, …

The virtual work that is done by the internal forces of the system is distinguished from that of the external forces. Helmholtz supposed that the internal force admits a force function – or potential energy – Φ; the work that this force does for a variation δp_a of one of the parameters is:

$$- \frac{d\Phi}{dp_a} \delta p_a \; .$$

As for the external force that results from that variation, it is denoted by:

$$- P_a \, \delta p_a \; .$$

With these new notations, the Lagrange equation that relates to the parameter p_a is:

(1)
$$\frac{d}{dt} \frac{dL}{dq_a} - \frac{dL}{dp_a} = - \frac{d\Phi}{dp_a} - P_a \; .$$

311. The potential energy Φ depends upon only the position of the molecules in the system; it is therefore a function of the parameters p, but not their derivatives q.

On the contrary, the kinetic energy L depends upon both the p and the q; it is homogeneous and of second degree with respect to the latter quantities. Indeed, L, which is equal to $\sum mv^2$, is of degree – 2 with respect to time; thus, if one doubles the unit of time then the value of L will be quadrupled. Now, p_a does not vary under that change of unit, while q_a must double; it is therefore necessary that each term in L must contain the q to the second degree.

As a result of that property of the function L, we will have:

(2)
$$2L = \sum q_a \frac{dL}{dq_a} \; .$$

312. Set:
(3)
$$H = \Phi - L$$
and
(4)
$$U = \Phi + L;$$

U is then the total energy of the system.

Upon differentiating the first of these equalities with respect to p_a, we will get:

$$\frac{dH}{dp_a} = \frac{d\Phi}{dp_a} - \frac{dL}{dp_a} \; ;$$

the derivation with respect to q_a gives us:

$$\frac{dH}{dq_a} = -\frac{dL}{dq_a},$$

since Φ does not depend upon the q. We infer the derivatives of L with respect to p_a and q_a from these equalities and then substitute the values that we found into equation (1); we will then have:

(5)
$$-\frac{d}{dt}\frac{dH}{dq_a} + \frac{dH}{dp_a} = -P_a.$$

Now set:

(6)
$$-\frac{dH}{dq_a} = \frac{dL}{dq_a} = s_a;$$

s_a and the quantities s_b, …, which are defined by analogous equations, are functions of the p and q. We can thus consider U to be a function of p and s, while H is always considered to be a function of the p and q. The equalities (3) and (4) give us:

$$U = H + 2L$$

for that function U, or, from the relations (2) and (6):

$$U = H + \sum q_a s_a.$$

It then results from that new equality, upon taking the total differential of the two sides, that:

$$\sum \frac{dU}{dp}dp + \sum \frac{dU}{ds}ds = \sum \frac{dH}{dp}dp + \sum \frac{dH}{dq}dq + \sum s\,dq + \sum q\,ds.$$

However, from (6):

$$\sum \frac{dH}{dq}dq = -\sum s\,dq;$$

consequently, the preceding equality will reduce to:

$$\sum \frac{dU}{dp}dp + \sum \frac{dU}{ds}ds = \sum \frac{dH}{dp}dp + \sum q\,ds.$$

We deduce from this that:

(7)
$$\frac{dU}{dp_a} = \frac{dH}{dp_a}$$

and

(8)
$$\frac{dU}{ds_a} = q_a.$$

313.   The expression for the principle of conservation of energy is deduced immediately from the relations (7) and (8). Those relations give us:

$$\frac{dU}{dp_a} = -\frac{ds_a}{dt} - P_a \; ,$$

$$\frac{dU}{ds_a} = q_a = \frac{dp_a}{dt} \; .$$

Consequently:

$$dU = \sum \frac{dU}{dp} dp + \sum \frac{dU}{ds} ds$$

$$= -\sum P \, dp - \sum \frac{ds}{dt} dp + \sum \frac{dp}{dt} ds \; ,$$

or

$$dU = -\sum P_a \, dp_a \; .$$

The variation of the total energy of the system is thus equal to the work that is done on the system by external forces; it is indeed the statement of the principle of the conservation of energy.

314. Hypotheses on the nature of the parameters. – Helmholtz assumed that the parameters that defined the situation of the system can be divided into two classes according to the manner by which they vary in time; those of the one class vary quite slowly, while those of the other vary quite rapidly. We denote the former parameters by p_a and the latter by p_b .

That hypothesis seems very natural. The molecular motions that are due to the heating of a body have velocities that are incomparably larger than the ones that we can communicate to the ensemble of the body. The parameters that define the relative positions of the molecules thus vary rapidly; on the contrary, the ones that fix the position of the body in space have a slow variation.

315. Helmholtz then made another hypothesis that might seem difficult to accept. He assumed that the function Φ did not depend upon the parameters p_b and that these parameters enter into the function L only by their derivatives q_b .

One can then give come simple examples from elementary mechanics in which that hypothesis is found to be realized.

Therefore, consider a pulley that moves around its axis. The position of the pulley can be defined by the angle p_b that a fixed plane in space makes with a plane that passes through a point of the pulley and its axis; p_b is then a system parameter. The semi-*vis viva* of the system is equal to the product of the moment of inertia of the pulley with the square of its angular velocity. The moment of inertia does not depend upon p_b . The angular velocity is $q_b = dp_b / dt$. As a result, the semi-*vis viva* depends upon only q_b and

not the parameter p_b . On the other hand, since the center of gravity of the pulley is on the rotational axis, the potential energy will not vary; it is therefore independent of the p_b.

Take another example. Consider a channel that is traversed by a liquid and suppose that the regime is established permanently. One can define the position of the system by the angle p_b that is defined by a diameter of the channel, which is fixed in space, and a diameter that passes through one of the liquid molecules. However, neither the potential energy not the kinetic energy will depend upon that parameter because those quantities remain constant. Indeed, once the permanent regime is established, a molecule will be immediately replaced with another one once the first one is displaced; in addition, the work that is done by internal forces is zero, and in turn, the potential energy will preserve the same value.

It results from these examples that the Helmholtz hypothesis is exact in the case of a body that rotates around an axis. It then seems applicable to the vortical motions of the molecules. Can it then be applied to the case in which the molecules of the body displace rectilinearly on one side and the other of a fixed point? That is what we shall examine later on.

316. We assume the Helmholtz hypothesis and continue to present the theory of that scholar.

Since Φ and L are assumed to be independent of the parameters p_b, H will not depend upon them either. From equation (5), we will then have:

$$(9) \qquad\qquad -\frac{d}{dt}\frac{dH}{dq_b} = -P_b \,,$$

or, from the definition of the functions s:

$$\frac{ds_b}{dt} = -P_b \,.$$

The external work that corresponds to the parameter considered is $-P_b\, dp_b$ for a variation dp_b of that parameter. When expressed as a function of the time interval dt, that variation will be $\dfrac{dp_b}{dt}dt$, or $q_b\, dt$. Consequently, the external work can be written $-P_b\, q_b\, dp_b$. Helmholtz set:

$$dQ_b = -P_b\, q_b\, dp_b \,.$$

If we replace P_b with its value that is inferred from the preceding equation in that equality then that will give:

$$(10) \qquad\qquad dQ_b = q_b\frac{ds_b}{dt}dt = q_b\, ds_b \,.$$

This is the equation that relates to the parameters that vary quite rapidly.

We now occupy ourselves with the slowly-varying parameters, and show that the derivative $\dfrac{d}{dt}\dfrac{dH}{dq_b}$ can be neglected for them.

From the equalities (6), we have:

$$\frac{dH}{dq_b} = -\frac{dL}{dq_b}.$$

Now, L is a homogeneous function of second degree with respect to the q_a and q_b ; $\dfrac{dH}{dq_a}$ will then be composed of terms of the form $A\, q_{a'}\, q_{a''}$ and $B\, q_{a'}\, q_b$. As a result, the derivative $\dfrac{d}{dt}\dfrac{dH}{dq_a}$ of that quantity with respect to time will contain only terms of the form:

$$A q_{a'} \frac{dq_{a'}}{dt}, \qquad B q_b \frac{dq_{a'}}{dt}, \qquad B q_{a'} \frac{dq_b}{dt}.$$

However, since the parameters p_a vary quite slowly, $q_{a'}$ and $q_{a''}$ will be very small, and the derivatives of these quantities with respect to t will likewise be very small; we can then neglect the terms of the first two forms, since they contain the product of two very small quantities. We can likewise neglect terms of the third form, but on the condition that we suppose that the derivative dq_b / dt of the finite quantity q_b is very small. (Therefore, if − to fix ideas − we return to the pulley that just served as an example for us then that will amount to supposing that the angular velocity of that pulley is very large, but reasonably constant.) Having assumed that hypothesis, all of the terms in $\dfrac{d}{dt}\dfrac{dH}{dq_a}$ will be negligible.

We will then have:

(11) $$\frac{dH}{dp_a} = -P_a ,$$

which is obtained by neglecting the first term in equation (5), as the equation that relates to the parameters p_a.

317. Monocyclic systems. – Helmholtz gave the name of *monocyclic systems* to the ones for which the number of rapidly-varying parameters reduces to 1; in the case where the number of these parameters is greater than 1, the system is *polycyclic*.

One has that dQ / L is an exact differential in all monocyclic systems.

In order to prove that property, first consider a monocyclic system whose situation is defined by just one rapidly-varying parameter that we can denote by p with no ambiguity.

In the relation (2):

$$2L = \sum q_a \frac{dL}{dq_a} ;$$

q_a denotes the derivative of an arbitrary parameter that varies rapidly or slowly. However, q_a is very small for the latter, and the terms that correspond to it can be neglected. All that then remains in the right-hand side is the term that corresponds to the parameter p; as a result:

$$(12) \qquad 2L = q \, \frac{dL}{dq} = q \, s.$$

From the relation (10), one will have for dQ:

$$dQ = q \, ds.$$

Consequently:

$$(13) \qquad \frac{dQ}{L} = \frac{2q \, ds}{qs} = 2d \log s;$$

the quotient considered is then an exact differential precisely.

318.   Incomplete systems. – Helmholtz divided the polycyclic or monocyclic systems into two classes: *complete systems* and *incomplete systems*. The latter are the ones for which the work $– P_a \, dp_a$ that corresponds to a non-zero variation of the one of the parameters p_a is equal to zero.

For these systems, from equation (11), one will have as many equations:

$$(14) \qquad \frac{dH}{dp_a} = 0$$

as there are parameters p_a that enjoy the preceding property. From the Helmholtz hypothesis, the function H does not depend upon the rapidly-varying parameters p_b, and the derivatives of the q_a can be neglected, so the equations that are analogous to (14) can be considered to be relations between the parameters p_c, the parameters p_a, and the derivatives q_b. Since they are the same in number as the parameters p_c, they can then serve for us to express those parameters as functions of the p_a and q_b. These parameters are thus not necessary in order to define the situation of the system; the parameters p_a (which are deduced from the ones that we just denoted by p_c) and the parameters p_b will suffice for that.

Will the equations be changed when one takes only the parameters p_a and p_b to be the independent variable?

Call the expression for H under those conditions H'. H' depends upon p_a and q_b; H depends upon p_a, p_c, and the q_b.

Since H' and H denote one and the same function when it is expressed in different variables, we will have:

$$H' = H.$$

Now, take the derivatives of the functions with respect to p_a; we will have:

$$\frac{dH'}{dp_a} = \frac{dH}{dp_a} + \sum \frac{dH}{dp_c}\frac{dp_c}{dp_a}.$$

Now, from the relation (14):

$$\frac{dH}{dp_c} = 0;$$

consequently:

$$\frac{dH'}{dp_a} = \frac{dH}{dp_a}.$$

The Lagrange equations that relate to the slowly-varying parameters thus keep the same form: viz., the form (11).

Take the derivative with respect to q_b ; we will get:

$$\frac{dH'}{dp_b} = \frac{dH}{dq_b} + \sum \frac{dH}{dp_c}\frac{dp_c}{dq_b},$$

and, in turn, for the same reason as before, we will get:

$$\frac{dH'}{dp_b} = \frac{dH}{dp_b}.$$

It results immediately from that equality and the equalities (6) that the function s_b remains the same regardless of whether the parameters p_c enter explicitly in the number of the ones that define the situation of the system or they do not take part in it. Consequently, in one case or the other, the Lagrange equations that relate to the rapidly-varying parameters will have the form (10):

$$dQ_b = q_b\, ds_b.$$

Since the form of the equations will remain the same, it is obvious that in the case of a monocyclic system, the factor $1/L$ will be an integrating factor for dQ.

319. The incomplete systems thus differ only slightly from the complete ones. Nevertheless, it is a property that is important to distinguish.

The kinetic energy L is, in general, a homogeneous function of second degree in the q_b and the q_a ; in addition, it depends upon the slowly-varying parameters. Now, we just saw that in the incomplete systems, one part of these parameters – viz., the parameters p_c – are function of the q_b and p_a . Consequently, if we replace the p_c with their expressions as functions of q_b in L then L will cease to be of second degree in the q_b . It can then be of odd degree with respect to these derivatives, and in turn, of odd degree with respect to time. We will soon see the importance of that remark.

The simplest example that one can cite is that of a pulley, on whose axis a regulator with the centrifugal force is mounted. When the velocity of the pulley increases, the balls of the regulator will rise, and the moment of inertia of the system will increase.

The *vis viva* is not proportional to the square of the angular velocity then, since it is equal to the product of that square with the moment of inertia, which varies with that velocity.

320. Application to calorific phenomena. – Assume, with Helmholtz, that the parameters p_b refer to the molecular motions that are due to heat, and the parameters p_a refer to the visible motions of the system.

As a result of that distinction between these diverse parameters, the equation:

$$dU = - \sum p_a \, dp_a$$

of paragraph **313** will become:

$$dU = - \sum p_a \, dp_a - \sum p_b \, dp_b$$

or

$$dU = - \sum p_a \, dp_a + \sum dQ_b \,.$$

Thus, from that relation, the variation of the internal energy is equal to the signed sum of the external work $\sum p_a \, dp_a$ that is done by the visible motion and the external work $- \sum dQ_b$ that is done by the molecular forces. Compare that expression for dU with the one that the principle of equivalence provides us with: The variation of the internal energy, when expressed in mechanical units, is the sum of the work and the heat dQ, when expressed in the same units, that are provided to the system. One sees that the two stated variations will become identical when one assumes that:

$$dQ = \sum dQ_b \,;$$

i.e., if one assumes that the external work that is done by molecular forces, with the sign changed, is equivalent to the heat that is provided to the body during the transformation. The principle of equivalence will thus reduce to the general principles of mechanics when one considers the bodies to be composed of molecules that act upon each other, but we already know that.

321. Now, consider a monocyclic system. In that case, we know that:

(15) $$\frac{dQ_b}{L} = \text{exact differential.}$$

However, dQ_b is nothing but the heat (when expressed in mechanical units) that is provided to the system, since $\sum dQ_b$ will reduce to dQ_b for a monocyclic system. In order to account for Carnot's principle, it will then suffice to suppose that the temperature of the system is proportional to the kinetic energy L. Since the terms in that energy that contain q_a are negligible, moreover, that energy can be confused with the molecular kinetic energy.

Is it possible to assume that the absolute temperature of a system is proportional to the molecular kinetic energy? The kinetic theory of gases shows that this is true for those bodies. As we just saw, Helmholtz's theory obliges us to assume that the same thing is still true for all other bodies.

From Carnot's principle, which is regarded as having been proved experimentally, set:

(16)
$$\frac{dQ}{T} = dS,$$

in which S is the product of the entropy with the equivalent mechanical work. Hence, $dQ = dQ_b \, dS$, and the differential (15) will be annulled at the same time. The latter is then a function of S; set:

$$\frac{Q_b}{L} = \varphi(S).$$

We then set:

$$\frac{dQ_b}{L} = \varphi'(S) \, dS = \varphi'(S) \frac{dQ}{T},$$

and in turn:

$$L = T \, \theta(S).$$

In order to determine θ, consider two systems for which the quantities L and S have the values L_1 and S_1 and L_2 and S_2, respectively.

We suppose that the two systems are at the same temperature T. That is necessary, since we would like to consider only reversible phenomena, for the moment.

We will then have:

$$L_1 = T \, \theta_1 (S_1), \qquad L_2 = T \, \theta_2 (S_2).$$

The values of these quantities for the ensemble of the two systems will be $L_1 + L_2$ and $S_1 + S_2$. We will then have:

$$L_1 + L_2 = T \, \theta_3 (S_1 + S_2),$$

and consequently:

$$\theta_1 (S_1) + \theta_2 (S_2) = \theta_3 (S_1 + S_2).$$

Differentiate the two sides of that equality by S_1; we will then have:

$$\theta_1' (S_1) = \theta_3' (S_1 + S_2),$$

and upon once more differentiating with respect to S_2:

$$0 = \theta_3'' \, (S_1 + S_2).$$

We then deduce the value of $\theta_3 \, (S_1 + S_2)$ from this:

$$\theta_3 \, (S_1 + S_2) = a + b \, (S_1 + S_2),$$

and as a result:

$$\theta_1 \, (S_1) = a' + b \, S_1 \, , \qquad \theta_2 \, (S_2) = a'' + b \, S_1 \, .$$

The three linear functions of θ_1, θ_2, θ_3 thus differ by only the constant terms a, a', or a'', but the coefficient b is the same for all of them.

Upon denoting the constants by a and b, we will then have that the former depends upon the nature of the body, while the latter is the same for all bodies:

$$L = T \, (a + b \, S).$$

We just saw that the coefficient b must have the same value for any body that one considers. As a result, b will be zero for all bodies, since that is true for gases. The absolute temperature is thus always proportional to the molecular kinetic energy.

322. Helmholtz's theory, applied to vibratory motions. – As we have remarked, Helmholtz's hypothesis (no. **318**) is justified only in the case of vorticial motion. Now, molecular motions seem to be vibratory motions about one side or the other of a fixed point. Is the quotient $dQ \, / \, T$ still an exact differential for this kind of motion? We shall show that this property persists in the case of monocyclic systems, even when one abandons the hypothesis of paragraph **315**.

If we abandon that hypothesis then the potential energy Φ will be a function of the rapidly-varying parameter p that we can write:

(17) $$\Phi = \frac{Ap^2}{2} + C,$$

in which A and C are functions of the p_a. Indeed, writing that equality amounts to neglecting the terms of higher degree than the second and suppressing the terms of first degree in the development of Φ in increasing powers of p. Now, the coefficients of the terms of degree higher than the second are necessarily very small, and we can neglect these terms. On the other hand, it is always possible to take the parameter p in such a way that it is zero when the molecule is at the mean of its oscillation; under those conditions, Φ will be of even degree with respect to p, and in turn, the first term of first degree will be zero.

The kinetic energy L is homogeneous and of second degree with respect to q and the q_a; we can then set:

(18) $$L = \frac{Bq^2}{2},$$

in which B denotes a function of the p_a, if we continue to suppose that the q_a are very small.

323. We seek the Lagrange equation that relates to the parameter p. From one of the equalities (6), we will have:

$$s = \frac{dL}{dq} = B\,q$$

and consequently, for the desired equation:

$$\frac{dBq}{dt} + \frac{dH}{dp} = -P.$$

However:

$$H = \Phi - L,$$

and in turn:

$$\frac{dH}{dp} = \frac{d\Phi}{dp} - \frac{dL}{dp} = A\,p\;;$$

the preceding equation can then be written:

(19) $$\frac{dBq}{dt} + Ap = -P.$$

If we suppose that the vibratory motion is stationary then P will be zero, and A and B will remain constant; consequently, that equation will become:

$$B\frac{dq}{dt} + Ap = 0,$$

or

$$B\frac{d^2 p}{dt^2} + Ap = 0.$$

If we set:

$$A = n^2 B$$

then one solution to that equation will be:

$$p = h\sin(nt + \omega);$$

we infer from this by derivation that:

$$q = hn\cos(nt + \omega),$$

and upon substituting that value q in the right-hand side of (18), we will get:

$$L = \frac{Bh^2 n^2 \cos^2 (nt + \omega)}{2} .$$

When one considers the system during a sufficiently long time with respect to the period of vibration, it will be the mean value of that quantity that intervenes; we must then take the expression:

(20)
$$L = \frac{Bh^2 n^2}{2} = \frac{Ah^2}{4}$$

to be the denominator of the ratio dQ / L.

324. Now, suppose that the slowly-varying parameters change in value; in other words, suppose that the vibratory motion is not stationary, so P is non-zero. Evaluate the work:

$$\delta Q = -\int P \, dp$$

that is provided by the exterior and relates to the rapidly-varying parameter during a time δt that is very small in absolute value, but nonetheless very large with respect to the period of vibration.

From equation (19), we will then have:

$$\delta Q = \int \frac{dB}{dt} q \, dp + \int B \frac{dq}{dt} dp + \int Ap \, dp .$$

The first of these integrals is performed easily. Since the function B depends upon only the slowly-varying parameters, its derivative with respect to t will be small and slowly-varying; we can then consider it to be constant, as the integral to be evaluated will become:

$$\frac{dB}{dt} \int q \, dp = \frac{dB}{dt} \int q^2 \, dt .$$

Since the integration is taken over a very small time interval δt, the preceding integral can be replaced with the product of δt with the mean value $h^2 n^2 / 2$ of q^2; we will then have:

$$\int \frac{dB}{dt} q \, dp = \frac{dB}{dt} \delta t \frac{h^2 n^2}{2} = h^2 n^2 \, \delta B,$$

in which δB denotes the variation of B during the time δt.

In order to get the other two integrals, develop A and B in increasing powers of t; upon supposing, for the moment, that we have taken the origin of time to be the start of the interval δt, we will then have:

$$A = A + \frac{dA}{dt}t + \frac{d^2A}{dt^2}t^2 \ldots,$$

$$B = B + \frac{dB}{dt}t + \frac{d^2B}{dt^2}t^2 \ldots$$

However, since the time interval δt during which one considers the system is very small, it is pointless to take into account the terms of second degree and higher in t; in addition, we can regard dA/dt and dB/dt as constants during that interval. We then get:

$$\int B\frac{dq}{dt}dp = \int Bq\,dq = B\int q\,dq + \frac{dB}{dt}\int tq\,dq,$$

$$\int Aq\,dq = A\int p\,dp + \frac{dA}{dt}\int tp\,dp$$

for the integrals to be evaluated.

325. We can choose the time interval δt in such a manner that p is zero at the start and finish of that interval; q will then be equal to nh at those two instants. Under those conditions:

$$B\int q\,dq = B\,d\,\frac{n^2h^2}{2}$$

and

$$A\int p\,dp = 0.$$

Upon integrating by parts, the other two integrals can be written:

$$\frac{dB}{dt}\int tq\,dq = \frac{dB}{dt}\left(\frac{tq^2}{2} - \int\frac{q^2}{2}dt\right),$$

$$\frac{dA}{dt}\int tp\,dp = \frac{dA}{dt}\left(tp^2 - \int\frac{p^2}{2}dt\right),$$

and one will easily see that the first of them has the value:

$$\frac{dB}{dt}\left(\delta t\,\frac{n^2h^2}{2} - \delta t\,\frac{n^2h^2}{4}\right) = \delta B\,\frac{n^2h^2}{4},$$

while the second one has the value:

$$\frac{dA}{dt}\left(0 - \delta t\, \frac{h^2}{4}\right) = -\,\delta A\, \frac{h^2}{4}\,.$$

Consequently, upon replacing the δQ in the integrals with their values, we will get:

$$\delta Q = \delta B\, \frac{n^2 h^2}{2} + B\delta\, \frac{n^2 h^2}{2} + \delta B\, \frac{n^2 h^2}{4} + \delta A\, \frac{h^2}{4}\,,$$

or

$$\delta Q = 3\,\delta B\, \frac{n^2 h^2}{4} + B\delta\, \frac{n^2 h^2}{2} - \delta A\, \frac{h^2}{4}\,.$$

Divide that equality L, whose values are given by the equalities (20); we will then have:

$$\frac{\delta Q}{L} = 3\frac{\delta B}{B} + 2\frac{\delta n^2 h^2}{n^2 h^2} - \frac{\delta A}{A}\,.$$

Since each of the terms in the right-hand side is the derivative of a logarithm, the sum of these terms is the derivative of the logarithm of the product; it is therefore an exact differential. Consequently, Clausius's theorem is also indeed proved in the case of a vibratory state of molecules, as well as in the case of a vorticial state.

326. Irreversible phenomena. – Let us return to Helmholtz's theory. First of all, it seems that it cannot take irreversible phenomena into account.

Consider the function H. As we know, it is a function of the p and q; the latter quantities enter into it in the second degree, since $H = \Phi - L$, and Φ does not depend upon the q, while L contains these quantities in the second degree. When one changes the sign of time – i.e., when one returns the system to its initial state – the p will not change sign, but the derivatives $q = dp\,/\,dt$ will change in sign. However, since these quantities appear in the second degree in H, the latter function will keep the same value. Now, the equations that define the state of the system at each instant can be put into the form (5):

$$-\frac{d}{dt}\frac{dH}{dq_a} + \frac{dH}{dp_a} = -P_a\,.$$

Its first term does not change in value when dt becomes negative, since dq_a changes in sign at the same time, and we just saw that H keeps the same value; as for the other terms, they will not change in value either. These equations will thus remain the same for any sign of dt. As a result, when the system returns to its initial state, it will again pass through precisely the same states that it took upon starting in the initial state; the transformations are thus reversible.

327.   However, we have see that in the case of incomplete systems, L can be expressed by a function that is of third degree in the q. As a result, L will change value with the sign of dt under these conditions. Irreversible phenomena can then take place with the incomplete systems; that is what Helmholtz assumed.

However, that illustrious physicist likewise appealed to another interpretation that is analogous, moreover.

Suppose that the quantities P_b are zero for some of the rapidly-varying parameters p_b ; we denote these parameters by the notation p_c . We will then have:

$$ds_c = \frac{dQ_c}{q_c} = - P_c \, dt = 0.$$

The s_c are thus constants that I call s_c^0 . The relations:

$$s_c = s_c^0$$

permit me to eliminate the quantities q_c and keep only the p_a and q_b (but not the q_c) as independent variables.

Now, denote the partial derivatives that are calculated with the old system of variables p_a, q_b, and q_c by d, and let δ denote the partial derivatives that are calculated with the new variables p_a and q_b .

Moreover, set:

$$H' = H + \sum s_c^0 q_c \; ;$$

one will get:

$$\frac{\partial H}{\partial p_a} = \frac{dH}{dp_a} + \sum \frac{dH}{dq_c}\frac{\partial q_c}{\partial p_a} = \frac{dH}{dp_a} - \sum s_c \frac{\partial q_c}{\partial p_a} = \frac{dH}{dp_a} - \sum s_c^0 \frac{\partial q_c}{\partial p_a},$$

$$\frac{\partial H'}{\partial p_a} = \frac{\partial H}{\partial p_a} + \sum s_c^0 \frac{\partial q_c}{\partial p_a},$$

so

$$\frac{\partial H'}{\partial p_a} = \frac{dH}{dp_a} .$$

Moreover, we will have:

$$\frac{\partial H}{\partial q_b} = \frac{dH}{dq_b} - \sum s_c^0 \frac{\partial q_c}{\partial q_b}$$

and

$$\frac{d}{dt}\frac{\partial H}{\partial q_b} = \frac{d}{dt}\frac{dH}{dq_b} - \sum s_c^0 \frac{d}{dt}\frac{\partial q_c}{\partial q_b} - \sum \frac{ds_c^0}{dt}\frac{\partial q_c}{\partial q_b},$$

and since:

$$s_c = s_c^0, \qquad \frac{ds_c}{dt} = 0,$$

it will become:

$$\frac{d}{dt}\frac{\partial H}{\partial q_b} = \frac{d}{dt}\frac{dH}{dq_b} - \sum s_c^0 \frac{d}{dt}\frac{\partial q_c}{\partial q_b}.$$

Likewise:

$$\frac{d}{dt}\frac{\partial H'}{\partial q_b} = \frac{d}{dt}\frac{\partial H}{\partial q_b} + \sum s_c^0 \frac{d}{dt}\frac{\partial q_c}{\partial q_b};$$

therefore:

$$\frac{d}{dt}\frac{\partial H'}{\partial q_b} = \frac{d}{dt}\frac{\partial H}{\partial q_b}.$$

Our equations then become:

$$\frac{\partial H'}{\partial p_a} = -P_a, \qquad d\frac{\partial H'}{\partial q_b} = -q_b\, dQ_b\,.$$

They thus keep the same form. If the number of rapidly-varying parameters other than the p_c is reduced by 1 then the systems will be monocyclic; however, the integrating factor will no longer be $1/L$, but $1/q_b\, s_c$.

The relations $s_c = s_c^0$ are not homogeneous with respect to q, since the left-hand side is of first degree and second has degree 0.

It then results from the elimination of the q_c that L will no longer be homogeneous of second degree in the q and that H can contain terms of odd degree with respect to these quantities.

The equations then cease to be reversible – i.e., to remain invariant when one changes the sign of the time.

Helmholtz referred to motions that correspond to the parameters p_b for which P_b is zero as *hidden motions*, so the irreversibility of the phenomena must then be attributed to the existence of hidden motions in the system. The simplest example of such a system is the Foucault pendulum. In that case, the hidden motion is that of the Earth; that is the motion that prevents the pendulum from passing through the positions that it previously occupied in the opposite sense and destroys the reversibility of the phenomenon.

328. That explanation of irreversible phenomena might seem satisfactory. In my view, it does not account for all of thermodynamic phenomena. Let me show you that.

Consider a system that is devoid of any external action. In this case, the P_a are zero, and we will get:

(21)
$$\frac{ds}{dt} + \frac{dH}{dp} = 0,$$

$$s = -\frac{dH}{dq}$$

for the equations that relate to one parameter, upon suppressing the indices.

From the relations (2), (3), and (4), we will have:

$$U = H + \sum q \frac{dL}{dq},$$

or, upon taking (6) into account:

$$U = H + \sum qs.$$

Consider U as a function of p and s; we will get:

$$\frac{dU}{dp} = \frac{dH}{dp},$$

$$\frac{dU}{ds} = q$$

for the partial derivatives of that function, or from equation (21) and the significance of q:

$$(22) \qquad \frac{dU}{dp} = -\frac{ds}{dt}, \qquad\qquad \frac{dU}{ds} = \frac{dp}{dt}.$$

Since the system is isolated, its entropy can diminish; as a result, ds / dt must be positive when t increases.

Now, we can consider S to be a function of s and p. We will then have:

$$\frac{dS}{dt} = \sum \left(\frac{dS}{ds} \frac{ds}{dt} + \frac{dS}{dp} \frac{dp}{dt} \right),$$

or, upon replacing ds / dt and dp / dt with their values that are inferred from equations (22):

$$\frac{dS}{dt} = \sum \left(\frac{dS}{ds} \frac{dU}{ds} - \frac{dS}{ds} \frac{dU}{dp} \right).$$

Consequently, the condition that the system must satisfy is:

$$(23) \qquad \sum \left(\frac{dS}{ds} \frac{dU}{ds} - \frac{dS}{ds} \frac{dU}{dp} \right) > 0,$$

and that inequality must be satisfied for all values of p and s.

We shall see that this is not always true.

329. Indeed, it is possible to imagine a system for which S passes through a maximum. Since S cannot decrease, that quantity will remain constant when it attains its maximum value, which is a value for which the system will be in equilibrium. We can suppose that this state corresponds to zero values of s and p, since if those variables have values s' and p' that are non-zero then it will suffice to set:

$$s = s' + s'', \qquad p = p' + p'',$$

and to take s'' and p'' be new variables for which the variables are zero in the equilibrium state. We can likewise suppose that U and S are zero for that state, since these functions contain an arbitrary constant.

Develop S in increasing powers of the variables.

The first term of that development will be zero, from the preceding hypothesis. The set of terms of first degree in s and p is also zero, since S will pass through a maximum when $s = p = 0$; for that reason, the set of terms of second degree will be negative. Consequently, if we neglect the terms of degree higher than second then S will be a negative quadratic form of s and t; we can thus decompose it into squares whose coefficients are all negative.

Likewise, develop the function U; the constant term in the development will be zero. The same thing will again be true for the set of terms of first degree. Indeed, since the system is in equilibrium:

$$\frac{ds}{dt} = 0 \qquad \text{and} \qquad \frac{dp}{dt} = 0,$$

and as a result of equation (22):

$$\frac{dU}{dp} = 0 \qquad \text{and} \qquad \frac{dU}{ds} = 0.$$

Upon neglecting the terms of degree higher than second in the development, U will then reduce to a quadratic form in s and p.

330. Since the functions S and U are quadratic, their partial derivatives with respect to the variables of first degree, and in turn, the left-hand side of the inequality (23), will be quadratic functions. In order for that inequality to always be satisfied, it is necessary that this quadratic function must be put into the form of a sum of squares whose coefficients are positive. It can then be annulled only for $s = p = 0$.

Now, consider the function $- U / S$. It is homogeneous and of degree zero in p and s. One can then multiply s and p by the same arbitrary factor without changing the value of that function. One can take advantage of always making these variables smaller than a certain quantity; i.e., a finite one. U and S will then finite for any given values of the variables, and $- U / S$ can become infinite only if S is zero. However, since S is a negative quadratic function, it cannot be annulled. Thus, $- U / S$ cannot become infinite, and it must present a maximum, which we denote by λ, for some system of values for s and p other than $s = p = 0$.

For these values of the variables that correspond to that maximum, one will have:

$$\frac{dU / ds}{dS / ds} = \frac{U}{S} = - \lambda;$$

as a result:

$$\frac{dU}{dS} = -\lambda \frac{dS}{ds}.$$

One similarly has:

$$\frac{dU}{dp} = -\lambda \frac{dS}{dp}.$$

If we substitute these values of dU / ds and dU / dp in the left-hand side of the inequality (23) then it will be annulled. The quadratic function that it is equal to can then be annulled for non-zero values of p and s. As a result, none of the coefficients of the squares are positive, and the function can be negative.

The Helmholtz equations can thus explain the increase in entropy that is produced in isolated systems that are subject to irreversible transformations.

It results from this that irreversible phenomena and Clausius's theorem cannot be explained by means of the Lagrange equations.

331. The explanation for reversible phenomena is still not complete. In particular, one must explain why there is no transfer of heat from one body to another when two bodies at the same temperature are in contact. One is indeed tempted to give an explanation. One compares the two bodies with two pulleys whose rotational velocities are equal. When one links these pulleys, there is no impact, and as a result, no transmission of *vis viva* from one to the other. When one puts the two bodies in contact, there are no longer any impacts between molecules, since they possess the same velocity in the two bodies, since the temperatures are the same. However, this explanation is far from satisfactory.

332. The work of Boltzmann. – To the names of Helmholtz and Clausius, we must add that of Boltzmann. Among the papers of the latter scholar on the subject that we are occupied with, we point out only his proof of the Helmholtz hypothesis.

Boltzmann once more separated the parameters of the system into two classes: viz., the slowly-varying parameters and the rapidly-varying ones, but he no longer supposed that H was independent of the latter. He decomposed the total system into a large number of systems for which the period was the same, but the phases were different. Upon considering that ensemble of systems, Boltzmann showed that everything happens as if H did not depend upon the rapidly-varying parameters; the Helmholtz hypothesis was thus found to be justified. From this viewpoint, the work of Boltzmann must be pointed out here.

333. All of the attempts of that nature must then be abandoned; the only ones that have any change of success are the ones that are founded upon the intervention of *statistical laws*, such as, for example, the kinetic theory of gases.

That viewpoint, which I shall not develop here, can be summarized in a somewhat vulgar fashion as follows:

Suppose that we would like to place of an oat grain in the midst of a pile of wheat; that would be easy. Suppose that we would then like to recover it and remove it; we could not succeed in doing that. For certain physicists, all irreversible phenomena are constructed from this model.

FIN