"L'intégrale des forces vives en Thermodynamique," J. math. pures et appl. **4** (1898), 5-19.

The *vis viva* integral in thermodynamics

By **P. DUHEM**

Translated by D. H. Delphenich

I. – Some systems that admit a *vis viva* integral.

In this article, which is a continuation of our "Commentaire aux principes de la Thermodynamique" ([1]) and our memoir that was entitled "Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimique" ([2]), we propose to study a system whose various parts are at different temperatures. In order to simplify the notation, we suppose that there exist only two such parts, which we denote by the indices 1 and 2, but the proof that we carry out will be completely independent of the number of these parts.

Part 1 will have an absolute temperature T_1. In addition, it will defined by the *normal* variables $\alpha_1, \beta_1, \ldots, \lambda_1$. As we have always done in questions of this type, we assume that if only T_1 varies then $\alpha_1, \beta_1, \ldots, \lambda_1$ will keep invariable values, while the various material elements that comprise part 1 will remain immobile.

Likewise, part 2 will be defined to have a temperature T_2 and the normal variables $\alpha_2, \beta_2, \ldots, \lambda_2$.

We suppose that k bilateral constraints:

$$(1) \qquad \begin{cases} M_1'\,\delta\alpha_1 + \cdots + P_1'\,\delta\lambda_1 + M_2'\,\delta\alpha_2 + \cdots + P_2'\,\delta\lambda_2 = 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ M_1^k\,\delta\alpha_1 + \cdots + P_1^k\,\delta\lambda_1 + M_2^k\,\delta\alpha_2 + \cdots + P_2^k\,\delta\lambda_2 = 0 \end{cases}$$

exist between these two parts, in which the coefficients $M_1^j, \ldots, P_1^j, M_2^j, \ldots, P_2^j$ are functions of the variables $\alpha_1, \ldots, \lambda_1, \alpha_2, \ldots, \lambda_2$, but not T_1, T_2.

The internal thermodynamic potential of the system has the form:

$$(2) \qquad \mathcal{F} = \mathcal{F}_1(\alpha_1, \beta_1, \ldots, \lambda_1, T_1) + \mathcal{F}_2(\alpha_2, \beta_2, \ldots, \lambda_2, T_2) + E\Psi(\alpha_1, \beta_1, \ldots, \lambda_1, \alpha_2, \beta_2, \ldots, \lambda_2).$$

$\mathcal{F}_1$ is the internal thermodynamic potential of part 1, considered in isolation.

([1]) Journal de Mathématiques pures et appliquées (4) **8** (1892), 269; **9** (1893), 292; **10** (1894), 203.

([2]) Mémoires de la Société des Sciences physiques et naturelles de Bordeaux (5) **2** (1896). Paris (A. Hermann), 1896.

$\mathcal{F}_2$ is the internal thermodynamic potential of part 2, considered in isolation.

$E\Psi$ is the potential for the interaction between bodies 1 and 2.

The conditions (1) give the k relations:

$$(3)\qquad \begin{cases} M_1^1\alpha_1' + \cdots + P_1^1\lambda_1' + M_2^1\alpha_2' + \cdots + P_2^1\lambda_2' = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ M_1^1\alpha_1' + \cdots + P_1^1\lambda_1' + M_2^1\alpha_2' + \cdots + P_2^1\lambda_2' = 0 \end{cases}$$

between the velocities α_1', β_1', …, λ_1', α_2', β_2', …, λ_2'.

Suppose that the system is devoid of any viscosity and friction; we will then have:

$$(4)\qquad \begin{cases} A_1 - \dfrac{\partial}{\partial\alpha_1}(\mathcal{F}_1 + E\Psi - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha_1'} + \Pi^1 M_1^1 + \cdots + \Pi^k M_1^k = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ L_1 - \dfrac{\partial}{\partial\lambda_1}(\mathcal{F}_1 + E\Psi - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda_1'} + \Pi^1 M_1^1 + \cdots + \Pi^k M_1^k = 0, \end{cases}$$

$$(4,\text{ cont.})\qquad \begin{cases} A_2 - \dfrac{\partial}{\partial\alpha_2}(\mathcal{F}_2 + E\Psi - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha_2'} + \Pi^1 M_2^1 + \cdots + \Pi^k M_2^k = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ L_2 - \dfrac{\partial}{\partial\lambda_2}(\mathcal{F}_2 + E\Psi - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda_2'} + \Pi^1 M_2^1 + \cdots + \Pi^k M_2^k = 0 \end{cases}$$

for the equations of motion of the system ([1]).

In these equations:

$\mathfrak{T}$ is the *vis viva* of the system.

A_1, …, L_1 are the actions that the foreign bodies exert upon the body 1.

A_2, …, L_2 are the actions that the foreign bodies exert upon the body 2.

Finally,

Π^1, Π^2, …, Π^k are quantities that depend upon:

$$\begin{matrix} \alpha_1, \dots, \lambda_1, T_1, & \qquad & \alpha_2, \dots, \lambda_2, T_2, \\ \alpha_1', \dots, \lambda_1', & \qquad & \alpha_2', \dots, \lambda_2', \end{matrix}$$

but not ([2]) the quantities:

([1]) "Commentaire aux principes de la Thermodynamique," Part II, Chapter III, no. 7, Journal de Mathématiques pures et appliquées (4) **10** (1894), 255.

([2]) For a proof of this point, see "Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques, Part I, Chapter I, § 4.

$$\alpha_1'', \ldots, \lambda_1'', \quad \alpha_2'', \ldots, \lambda_2''.$$

The number of equations of motion (3), (4), (4, cont.) is $(n_1 + n_2 + k)$, if n_1 denotes the number of normal variables $\alpha_1, \beta_1, \ldots, \lambda_1$, and n_2 denotes the number of normal variables $\alpha_2, \beta_2, \ldots, \lambda_2$.

On the other hand, we have to determine:

the $(n_1 + 1)$ variables $\alpha_1, \beta_1, \ldots, \lambda_1, T_1$,
the $(n_2 + 1)$ variables $\alpha_2, \beta_2, \ldots, \lambda_2, T_2$,
the k auxiliary variables $\Pi_1, \Pi_1, \ldots, \Pi_1$,

as functions of time t.

Hence, there are $(n_1 + n_2 + k + 2)$ variables, in all.

One then has the following proposition:

The number of equations that thermodynamics provides in order to determine the motion of a system is less than the number of variables that it takes to determine all of the units in the system of the parts that are susceptible to being brought to different temperatures.

In order to complete the formulation of the dynamical problem in terms of equations, one must include a number of supplementary relations that are equal in number to those parts, along with the hypotheses that are foreign to thermodynamics.

Let:

$$(5) \qquad \theta_1 = 0, \qquad \theta_2 = 0$$

be these supplementary relations.

Multiply both sides of equations (4) by $\alpha_1', \beta_1', \ldots, \lambda_1'$, and both sides of equations (4, cont.) by $\alpha_2', \beta_2', \ldots, \lambda_2'$, respectively. Add the corresponding sides of the results thus-obtained, while taking the equalities (3) into account. We will find:

$$A_1\alpha_1' + \ldots + L_1\lambda_1' + A_2\alpha_2' + \ldots + L_2\lambda_2'$$
$$-\left(\frac{\partial \mathcal{F}_1}{\partial \alpha_1}\alpha_1' + \cdots + \frac{\partial \mathcal{F}_1}{\partial \lambda_1}\lambda_1' + \frac{\partial \mathcal{F}_2}{\partial \alpha_2}\alpha_2' + \cdots + \frac{\partial \mathcal{F}_2}{\partial \lambda_2}\lambda_2'\right) - E\frac{d\Psi}{dt} - \frac{d\mathfrak{T}}{dt} = 0.$$

Suppose that the actions that are exerted upon the system by the bodies that are foreign to the system depend upon a potential:

$$\Omega(\alpha_1, \ldots, \lambda_1, \alpha_2, \ldots, \lambda_2).$$

The preceding equality will become:

$$(6) \qquad \frac{d}{dt}(\Omega + \mathcal{F}_1 + \mathcal{F}_2 + E\Psi + \mathfrak{T}) - \frac{\partial \mathcal{F}_1}{\partial T_1}\frac{dT_1}{dt} - \frac{\partial \mathcal{F}_2}{\partial T_2}\frac{dT_2}{dt} = 0.$$

In order for the relation (6) *to immediately yield a first integral* (viz., a *VIS VIVA* INTEGRAL) *of the second-order equations* (4) *and* (4, cont.), *it is necessary and sufficient that the expression:*

$$\frac{\partial \mathcal{F}_1}{\partial T_1} dT_1 + \frac{\partial \mathcal{F}_2}{\partial T_2} dT_2$$

must represent the total differential of a function of $\alpha_1, \ldots, \lambda_1, \alpha_2, \ldots, \lambda_2, T_1, T_2$, *either by itself or by virtue of the supplementary equations* (5).

II. – Some classical systems.

The function $\mathcal{F}_1$ depends upon only the variables $\alpha_1, \beta_1, \ldots, \lambda_1, T_1$; the function $\mathcal{F}_1$ depends upon only the variables $\alpha_2, \beta_2, \ldots, \lambda_2, T_2$. In order for the expression:

$$\frac{\partial \mathcal{F}_1}{\partial T_1} dT_1 + \frac{\partial \mathcal{F}_2}{\partial T_2} dT_2$$

to be a total differential in its own right, it is necessary and sufficient that $\frac{\partial \mathcal{F}_1}{\partial T_1}$ must be a function of only the variable T_1 and that $\frac{\partial \mathcal{F}_2}{\partial T_2}$ must be a function of only the variable T_2. Therefore:

In order for a system that is subject to external actions that are derived from a potential to admit a vis viva integral, no matter what form the supplementary relations might take, it is necessary and sufficient that one must have:

$$(7) \qquad \begin{cases} \mathcal{F}_1(\alpha_1, \ldots, \lambda_1, T_1) = \mathcal{G}_1(T_1) + E\psi_1(\alpha_1, \ldots, \lambda_1), \\ \mathcal{F}_2(\alpha_2, \ldots, \lambda_2, T_2) = \mathcal{G}_2(T_2) + E\psi_2(\alpha_2, \ldots, \lambda_2). \end{cases}$$

We give the name of *classical systems* to the systems for which the equalities (7) are verified and which are devoid of any viscosity or friction.

We shall give an example of such a system; that example will justify the terminology of *classical system* that we have attributed to them.

Imagine an arbitrary number of bodies c_1, c_1', c_1'', … that all have the same temperature T_1, which varies from one instant to another. Suppose that each of these bodies is an invariable solid whose state is invariable, except for temperature. The internal thermodynamic potential of each of them is a function of only the temperature; let $g_1(T_1)$, $g_1'(T_1)$, $g_1''(T_1)$, … denote the internal thermodynamic potentials of the bodies c_1, c_1', c_1'', …

In order to form the partial system 1, take the bodies c_1, c_1', c_1'', …, and let them be independent of each other, or even linked by bilateral constraints with neither viscosity not friction. The partial system 1 will then be a system without viscosity or friction. If we let $\alpha_1, \beta_1, \ldots, \lambda_1$ denote the independent variables that fix the relative position of the bodies c_1, c_1', c_1'', … then the internal thermodynamic potential of the partial system 1 will be:

$$\mathcal{F}_1(\alpha_1, \beta_1, \ldots, \lambda_1, T_1) = g_1(T_1) + g_1'(T_1) + g_1''(T_1) + \ldots + E\psi_1(\alpha_1, \beta_1, \ldots, \lambda_1),$$

in which $E\psi_1(\alpha_1, \beta_1, \ldots, \lambda_1)$ is the potential of the interactions between the bodies c_1, c_1', c_1'', …

That internal thermodynamic potential has the form that was presented in the first equality (7).

Form the partial systems 2, … in a similar manner, and let them be independent of each other, or maybe associated by some bilateral constraints without viscosity or friction; one will obtain a classical system.

Moreover, one indeed sees that such a system, for which one can attribute very small dimensions to the bodies c_1, c_1', c_1'', … of the kind that some schools attribute to *molecules*, constitute just the general type of systems that one considered in mechanics before the recent epoch, during which thermodynamics is a venue that enlarged the scope of that science.

Let us examine the properties that thermodynamics attributed to these classical systems. That examination is important for the fact that it informs us of the links that unite the old mechanics with the new thermodynamics.

We have seen, first of all, that *in order for a classical system to admit a vis viva integral, it is necessary and sufficient that it must be subject to external actions that are derived from a potential* Ω.

Indeed, let $G_1(T_1)$, $G_2(T_2)$, … denote the functions that are defined by the equalities:

$$\frac{dG_1(T_1)}{dT_1} = \mathcal{G}_1(T_1), \qquad \frac{dG_2(T_2)}{dT_2} = \mathcal{G}_2(T_2), \qquad \ldots \tag{8}$$

By virtue of the equalities (7) and (8), the equality (6) will become:

$$\frac{d}{dt}(\Omega + \mathcal{F}_1 + \mathcal{F}_2 - \mathcal{G}_1 - \mathcal{G}_2 + E\Psi + \mathfrak{T}) = 0, \tag{9}$$

or then again:

$$\frac{d}{dt}[\Omega + E\,(\psi_1 + \psi_2 + \Psi) + \mathfrak{T}] = 0. \tag{10}$$

We then apply this last formula to the example of the classical system that we just defined.

In that case, $E(\psi_1 + \psi_2 + \Psi)$ will be the potential of all the actions that bodies c_1, c_1', c_1'', …, c_2, c_2', c_2'', … exert upon each other. The equality (10) will then lead to the following proposition for such a system:

The sum of the vis viva, the potential of the external actions, and the potential of the internal actions will remain invariable under any motion of the system.

One recovers the statement of the *vis viva* theorem as it is given in classical mechanics.

The internal energy U of a system is given, in general, by the formula:

$$EU = \mathcal{F} - T_1 \frac{\partial \mathcal{F}_1}{\partial T_1} - T_2 \frac{\partial \mathcal{F}_2}{\partial T_2}.$$

By virtue of equalities (2) and (7), this equality will become:

$$(11) \qquad EU = E(\psi_1 + \psi_2 + \Psi) + \mathcal{G}_1(T_1) - T_1 \frac{d\mathcal{G}_1(T_1)}{dT_1} + \mathcal{G}_2(T_2) - T_2 \frac{d\mathcal{G}_2(T_2)}{dT_2}$$

for a classical system. Set:

$$(12) \qquad EA(T_1, T_2) = \mathcal{G}_1(T_1) - T_1 \frac{d\mathcal{G}_1(T_1)}{dT_1} + \mathcal{G}_2(T_2) - T_2 \frac{d\mathcal{G}_2(T_2)}{dT_2},$$

so the preceding equality will become:

$$(13) \qquad U = \psi_1 + \psi_2 + \Psi + A(T_1, T_2).$$

By virtue of equalities (7) and (11), equations (4) and (4, cont.) will take the following form, which will thus constitute an acceptable form for the equations of motion of a classical system:

$$(14) \qquad \begin{cases} A_1 - \dfrac{\partial}{\partial \alpha_1}(EU - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha_1'} + \Pi^1 M_1^1 + \cdots + \Pi^k M_1^k = 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\ L_1 - \dfrac{\partial}{\partial \lambda_1}(EU - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda_1'} + \Pi^1 P_1^1 + \cdots + \Pi^k P_1^k = 0, \end{cases}$$

$$
(14, \text{cont.}) \quad \begin{cases}
A_2 - \dfrac{\partial}{\partial \alpha_2}(EU - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha_2'} + \Pi^1 M_2^1 + \cdots + \Pi^k M_2^k = 0, \\
\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\
L_2 - \dfrac{\partial}{\partial \lambda_2}(EU - \mathfrak{T}) - \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda_2'} + \Pi^1 P_2^1 + \cdots + \Pi^k P_2^k = 0.
\end{cases}
$$

In the equations of motion of a classical system, one can substitute the product of the internal energy with the mechanical equivalent of heat for the internal thermodynamic potential of the system.

We have already pointed out ([1]) that the equations of motion of the system that one studies in mechanics can be put into the form (14) and (14, cont.).

The caloric coefficients of a system with bilateral constraints are given by the equalities ([2]):

$$
(15) \quad \begin{cases}
E\dfrac{\partial U}{\partial \alpha_1} - \dfrac{\partial \mathfrak{T}}{\partial \alpha_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \alpha_1'} - A_1 - \Pi^1 M_1^1 - \cdots - \Pi^k M_1^k = ER_{\alpha_1}, \\
\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots, \\
E\dfrac{\partial U}{\partial \lambda_2} - \dfrac{\partial \mathfrak{T}}{\partial \lambda_1} + \dfrac{d}{dt}\dfrac{\partial \mathfrak{T}}{\partial \lambda_1'} - L_1 - \Pi^1 P_2^1 - \cdots - \Pi^k P_2^k = ER_{\lambda_1}, \\
E\dfrac{\partial U}{\partial T_2} = Ec_2.
\end{cases}
$$

By virtue of equalities (11), (14), (14, cont.), these equalities become:

$$
(16) \qquad R_{\alpha_1} = 0, \qquad \dots, \qquad R_{\lambda_1} = 0, \qquad R_{\alpha_2} = 0, \qquad \dots, \qquad R_{\lambda_2} = 0,
$$

$$
(17) \quad \begin{cases}
Ec_1 = -T_1 \dfrac{d^2 \mathcal{G}_1(T_1)}{dT_1^2}, \\
Ec_2 = -T_2 \dfrac{d^2 \mathcal{G}_2(T_2)}{dT_2^2}.
\end{cases}
$$

For a classical system all of the caloric coefficients are zero, except for the caloric capacity of each of the parts that have uniform temperature; that caloric capacity is a function of only temperature.

We have already pointed out ([1]) the exceptional role that is played by the systems that are characterized by the equalities in the definition of entropy.

([1]) "Commentaire aux principes de la Thermodynamique," Part I, Chapter III, no. 4, Journal de Mathématiques pures et appliquées (4) **8** (1892), 324.

([2]) "Commentaire aux principes de la Thermodynamique," Part III, Chapter III, no. 8, Journal de Mathématiques pures et appliquées (4) **10** (1894), 324.

The quantity of heat δQ that the system releases during an arbitrary real or virtual modification will have the value:

(18) $$\delta Q = -(c_1\,\delta T_1 + c_2\,\delta T_2),$$

or even, by virtue of equalities (12) and (17):

(19) $$\delta Q = -\,\delta A\,(T_1, T_2).$$

The quantity of heat that is released by the system during an arbitrary real or virtual modification is the total differential of a uniform function of the state of the system.

Here, the function $A\,(T_1, T_2)$ plays exactly the role that the old physicists called the *quantity of free caloric* that is contained in the system. Moreover, for those physicists, the *quantity of latent caloric* that is contained in our system would be invariable.

By virtue of equalities (7), which characterize a classical system, the equations of motion (4) and (4, cont.) will become:

(20) $$\begin{cases} A_1 - \dfrac{\partial}{\partial\alpha_1} E(\psi_1+\Psi) + \dfrac{\partial\mathfrak{T}}{\partial\alpha_1} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha_1'} + \Pi^1 M_1^1 + \cdots + \Pi^k M_1^k = 0, \\ \dotfill, \\ L_1 - \dfrac{\partial}{\partial\lambda_1} E(\psi_1+\Psi) + \dfrac{\partial\mathfrak{T}}{\partial\lambda_1} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda_1'} + \Pi^1 P_1^1 + \cdots + \Pi^k P_1^k = 0, \end{cases}$$

(20, cont.) $$\begin{cases} A_2 - \dfrac{\partial}{\partial\alpha_2} E(\psi_1+\Psi) + \dfrac{\partial\mathfrak{T}}{\partial\alpha_2} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\alpha_2'} + \Pi^1 M_2^1 + \cdots + \Pi^k M_2^k = 0, \\ \dotfill, \\ L_2 - \dfrac{\partial}{\partial\lambda_2} E(\psi_1+\Psi) + \dfrac{\partial\mathfrak{T}}{\partial\lambda_2} - \dfrac{d}{dt}\dfrac{\partial\mathfrak{T}}{\partial\lambda_2'} + \Pi^1 P_2^1 + \cdots + \Pi^k P_2^k = 0, \end{cases}$$

These equations show us, in the first place, that in order to treat the motion of the system that we have chosen to be an example of a classical system, one can substitute the potential of the internal actions of each of the partial systems 1 and 2 for the internal thermodynamic potential of each of those partial systems in the equations of motion that are provided by thermodynamics; one will then recover the well-known equations of dynamics. However, equations (20) and (20, cont.) lead to a consequence that is more general since it applies to all classical systems:

The $(n_1 + n_2)$ equations (20) and (20, cont.), when combined with the k equations (3), can be regarded as $(n_1 + n_2 + k)$ linear equations in the $(n_1 + n_2 + k)$ unknowns:

([1]) "Commentaire aux principes de la Thermodynamique," Part II, Chapter III, no. 6, Journal de Mathématiques pures et appliquées (4) **9** (1893), 357.

$$\alpha_1'', \ldots, \lambda_1'', \quad \alpha_2'', \ldots, \lambda_2'',$$
$$\Pi^1, \Pi^2, \ldots, \Pi^k.$$

These $(n_1 + n_2 + k)$ unknowns are determined as functions of the coefficients of the $(n_1 + n_2 + k)$ linear equations. Now, the temperatures T_1, T_2 of the various parts of the system do not enter into any of these coefficients. We can then state the following proposition, in particular:

The quantities Π^1, Π^2, …, Π^k are independent of the temperatures T_1, T_2 of the various parts of the system.

That proposition implies the following one, in turn:

When the system being studied is a classical system, one can write the $(n_1 + n_2 + k)$ *differential equations* (3), (20), *and* (20, cont.) *in the* $(n_1 + n_2)$ *unknown functions* $\alpha_1(t)$, …, $\lambda_1(t)$, $\alpha_2(t)$, …, $\lambda_2(t)$, *and the k auxiliary unknown functions* Π^1, Π^2, …, Π^k, *in which the temperatures of the various parts of the system do not appear. Apart from any supplementary relation, these equations suffice to determine the laws by which the system is displaced and modified, with the exception of the law by which the temperature of each part of the system varies.*

Once the motion of the system is known, the supplementary relations will determine the law by which the temperature of each part varies.

One thus understands how Lagrange could develop the laws of mechanics of systems that were composed of solids without concerning himself with the variations of the temperatures of those bodies, and Fourier treated the variations of the temperatures of those solid bodies without concerning himself with their motions. That is how one can study the motion of the Earth, when it is assimilated to a rigid solid, without being preoccupied with the temperature of that astral body, and how one can study the cooling of the terrestrial globe without being preoccupied with its motion.

Such an independence of the problems that relate to mechanics from the problems that relate to the theory of heat will exist only when the systems that one deals with are no longer *classical systems*. For example, if instead of regarding the Earth as a rigid solid with an invariable state, one takes into account the changes in volume, form, and physical and chemical state that accompany its cooling then one can no longer separate the problem of the motion of the Earth from the problem of terrestrial cooling.

III. – Some systems that admit a *vis viva* integral by virtue of supplementary relations.

When one is not dealing with a classical system, the expression:

$$\frac{\partial \mathcal{F}_1(\alpha_1, \ldots, \lambda_1, T_1)}{\partial T_1} dT_1 + \frac{\partial \mathcal{F}_2(\alpha_2, \ldots, \lambda_2, T_2)}{\partial T_2} dT_2$$

will no longer be a total differential. However, it can happen that the supplementary equations (5) will imply an equality of the form:

(21)
$$\frac{\partial \mathcal{F}_1}{\partial T_1}\frac{dT_1(t)}{dt} + \frac{\partial \mathcal{F}_2}{\partial T_2}\frac{dT_2(t)}{dt} = \frac{dF(t)}{dt}.$$

In that case – and only in that case – the system will admit a *vis viva* integral, which will have the form:

(22)
$$\Omega + \mathcal{F}_1 + \mathcal{F}_2 + E\Psi + \mathfrak{T} - F(t) = \text{const.}$$

One can imagine an infinitude of forms for the supplementary relations (5) for which an equality of the form (21) is verified; we shall cite some remarkable examples.

Imagine that the supplementary relations (5) imply the consequence that:

Any modification of the system being studied is adiabatic.

Since the system is devoid of viscosity, the quantity of heat that is released by a real or virtual modification will have the value:

$$\delta Q = -(R_{\alpha_1}\delta\alpha_1 + \cdots + R_{\lambda_1}\delta\lambda_1 + c_1\delta T_1 + R_{\alpha_2}\delta\alpha_2 + \cdots + R_{\lambda_2}\delta\lambda_2 + c_2\delta T_2),$$

with

(23)
$$\begin{cases} R_{\alpha_1} = -\dfrac{T_1}{E}\dfrac{\partial^2 \mathcal{F}_1}{\partial \alpha_1 \partial T_1}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ R_{\lambda_1} = -\dfrac{T_1}{E}\dfrac{\partial^2 \mathcal{F}_1}{\partial \lambda_1 \partial T_1}, \\ c_1 = -\dfrac{T_1}{E}\dfrac{\partial^2 \mathcal{F}_1}{\partial T_1^2}, \end{cases}$$

(23, cont.)
$$\begin{cases} R_{\alpha_1} = -\dfrac{T_2}{E}\dfrac{\partial^2 \mathcal{F}_1}{\partial \alpha_2 \partial T_2}, \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, \\ R_{\lambda_2} = -\dfrac{T_2}{E}\dfrac{\partial^2 \mathcal{F}_1}{\partial \lambda_2 \partial T_2}, \\ c_2 = -\dfrac{T_2}{E}\dfrac{\partial^2 \mathcal{F}_2}{\partial T_2^2}. \end{cases}$$

We say that, as a result of equations (5), any real or virtual modification will be adiabatic; i.e., that equations (5) will imply the equality:

$$\frac{T_1}{E}\left(\frac{\partial^2 \mathcal{F}_1}{\partial \alpha_1\, \partial T_1}\alpha_1' + \cdots + \frac{\partial^2 \mathcal{F}_1}{\partial \lambda_1\, \partial T_1}\lambda_1' + \frac{\partial^2 \mathcal{F}_1}{\partial T_1^2}T_1'\right)$$
$$+ \frac{T_2}{E}\left(\frac{\partial^2 \mathcal{F}_2}{\partial \alpha_2\, \partial T_2}\alpha_2' + \cdots + \frac{\partial^2 \mathcal{F}_2}{\partial \lambda_2\, \partial T_2}\lambda_2' + \frac{\partial^2 \mathcal{F}_2}{\partial T_2^2}T_2'\right) = 0,$$

which can be further written:

$$\frac{\partial \mathcal{F}_1}{\partial T_1}\frac{dT_1}{dt} + \frac{\partial \mathcal{F}_2}{\partial T_2}\frac{dT_2}{dt} = \frac{d}{dt}\left(T_1 \frac{\partial \mathcal{F}_1}{\partial T_1} + T_2 \frac{\partial \mathcal{F}_2}{\partial T_2}\right).$$

That equality will take the form (21) if one sets:

$$F = T_1 \frac{\partial \mathcal{F}_1}{\partial T_1} + T_2 \frac{\partial \mathcal{F}_2}{\partial T_2}.$$

There then exists a *vis viva* integral, which is, by virtue of the equality (22):

$$\Omega + \mathcal{F}_1 - T_1 \frac{\partial \mathcal{F}_1}{\partial T_1} + \mathcal{F}_2 - T_2 \frac{\partial \mathcal{F}_2}{\partial T_2} + E\Psi + \mathfrak{T} = \text{const.},$$

or rather:

$$\Omega + EU + \mathfrak{T} = \text{const.},$$

which is a relation that follows immediately from the principle of the conservation of energy for an adiabatic modification that is accomplished as a result of external actions that are derived from a potential.

One of the forms of the complementary equations that imply the consequences that we have just detailed is obtained by expressing the idea that *each of the parts that it is composed of does not receive or give up any heat during a real modification of the system;* i.e., upon writing that one has:

$$R_{\alpha_1}\alpha_1' + \ldots + R_{\lambda_1}\lambda_1' + c_1 T_1' = 0,$$
$$R_{\alpha_1}\alpha_2' + \ldots + R_{\lambda_1}\lambda_2' + c_2 T_2' = 0,$$

or rather, by virtue of equalities (23) and (23, cont.):

$$\frac{d}{dt}\frac{\partial \mathcal{F}_1}{\partial T_1} = 0, \qquad \frac{d}{dt}\frac{\partial \mathcal{F}_2}{\partial T_2} = 0.$$

These are precisely the supplementary relations that were introduced by Laplace in his theory of the propagation of sound in a mass of air.

One will further obtain a relation of the form (21) if one takes the relations:

$$\frac{dT_1}{dt} = 0, \qquad \frac{dT_2}{dt} = 0$$

for the supplementary relations, or in other words, *if one supposes that each part of the system keeps an invariable temperature while the system is being modified.* One will then have:

$$F(t) = 0,$$

and the *vis viva* integral (22) will take the form:

$$\Omega + \mathcal{F}_1 + \mathcal{F}_2 + E\Psi + \mathfrak{T} = \text{const.},$$

which will then be the form of the *vis viva* integral for *isothermal modifications.*

One knows that this form for the supplementary relations ([1]) was introduced by Newton and the geometers of the 18th Century in the theory of sound.

These considerations show that the questions that relate to thermodynamics will have to come to the attention of physicists before they can begin the study of systems other than classical systems, and in fact, it was the theory of the propagation of sound in air that provoked Laplace to create thermodynamics.

____

([1]) On the subject of these two forms for the supplementary relations, see L. NATANSON, Zeitschrift für physikalische Chemie **24** (1897), 302.