On the mechanical foundations of thermodynamics

By Paul Hertz

Translated by D. H. Delphenich

———

Contents

———

Part II.

Thermo-mechanical processes

(The law of increasing entropy)

§ 10. External coordinates (equation of state)

One of the advantages of the **Lagrange** method is that it relieves us of having to specify the coupling equations. In fact, the generalized coordinates are chosen such that it is not necessary for one to exhibit the condition equations between them. However, we often encounter *condition inequalities* in the applications. For example, the molecule in a gas can be enclosed in a container in such a way that the position of the molecule cannot go beyond the space in the container. Now, it would be essential for our considerations for the system in each state to follow a path that corresponds to the direction of its velocity, so the path curve would possess no kink, and therefore all ε^*-surfaces that occur would be closed and rounded everywhere. Admittedly, that is not the case for the example that was just given, since the molecule will change its direction discontinuously at the wall. If one thinks of, e.g., a "one-dimensional gas" (Fig. 4a) – i.e., a single material point that cannot leave a line segment – and appeals to **Cartesian** coordinates then the ε^*-curve will consist of two separate pieces (Fig. 4b).
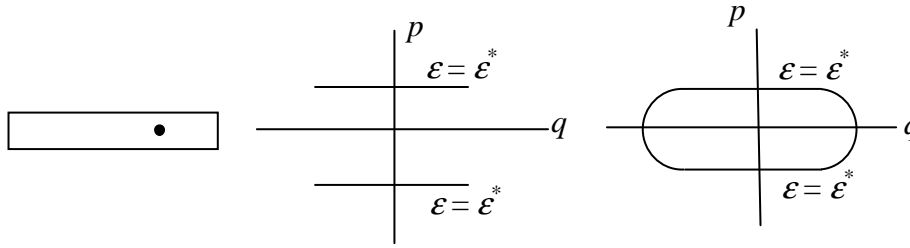
Figure 4a.   Figure 4b.   Figure 4c.

If we would now like to extend our analysis to all of these cases then we would need only to assume that there is a potential energy between the walls of the container and the molecules. It would then be unnecessary to impose any sort of restriction on the mass points. The penetration of a molecule into the wall is also possible, although such an exceeding of the normal bounds would be linked with the appearance of a significant amount of potential energy. Furthermore, since under these circumstances, the wall cannot define an absolute obstacle, all path curves will have to be continuous and nowhere have a sharp kink. That would also correspond to the ε^*-surface appearing to be closed and rounded. In the cases that we have been concerned with, the ε^*-curve might perhaps take the form that is suggested in Fig. 4c. In order to ultimately arrive at the ideal limiting case of absolute rigidity, one needs only to assume that the potential energy will also become exceedingly large for even the slightest penetration of the surface of the wall. It will then be impossible for the molecule to penetrate very far into the wall for finite initial energies. Nevertheless, one can choose all of infinite space to be the domain of variation of the coordinates, and thus free oneself of the condition equations. The choice of the potential energy will then also have the effect that the position of the molecule is restricted in practice to the interior of the container without assuming such inequalities.

The same argument will be true when the wall of the container is moving. We would like to call such a moving container wall a *piston*. Since the piston is moving, we must next treat the coordinates that determine it just like any other coordinates of the system and assume that they are likewise subject to a continual change. Later, it will be shown that those fluctuations are extremely minor, and that will give us the right to make an exception for those coordinates.

We would like to consider an entirely special case in these paragraphs. Let the container be a rectangular cylinder that is bounded by two congruent surfaces of area B that amount to the lid or piston and the base. Let the piston move freely. Its position will be determined by the coordinate a, namely, the volume between the base, the piston, and the outer surface of the cylinder. A pressure h acts on a unit area, so the potential energy will be:

$$U = k \cdot h \cdot B,$$

in which:

$$h = \frac{a}{B}$$

means the height of the piston above the base. One therefore also has:

(145) $$U = k\,a.$$

We would like to apply (42). That equation will give us:

(146) $$a\overline{\frac{\partial \varepsilon}{\partial a}} = \tfrac{1}{2}\,\mathrm{t}.$$

One must then address the determination of $\partial \varepsilon / \partial a$. Now, the potential energy also contains a component that originates in the molecules that are found to be in direct contact with the piston, which is a summand that changes with a in a manner that is not easy to recognize. In order to confront that difficulty, we assume generalized coordinates. We next choose a **Cartesian** coordinate cross whose z-axis runs perpendicular to the plane of the piston, and set:

(147) $$\begin{cases} q_{3i-2} = x_i, \\ q_{3i-1} = y_i, \\ q_{3i} \;= \varphi_i(z_i, a), \end{cases}$$

(148) $$h = \frac{a}{B},$$

(149a) $$\varphi_i = \frac{z_i}{h} \qquad\qquad (z_i < h),$$

(149b) $$\varphi_i = 1 + (z_i - h) \qquad (z_i > h).$$

These formulas shall be true everywhere, except in the immediate vicinity of $z_i = h$. Here, they shall be replaced with functional relations that will mediate a continuous transition to the differential quotients. However, that transition shall take place along a line segment that is extremely small, even in comparison to the small line segment that a molecule can penetrate into the piston, without provoking any appreciable potential energy.

If we change the q then the potential energy between the piston and molecule will change. By contrast, it will remain unchanged when the q remains constant. In fact, if we go to another value of a, while fixing the q, then, from (149), we will come to a new state in which one finds just as many molecules as before in the container's interior, and in which the molecules will penetrate just as deeply into the piston as before. If one would then like to calculate $\partial \varepsilon / \partial a$, where the partial differentiation with respect to a is performed with constant q, then one can ignore the potential energy between the piston and the molecule.

Now, from (147) to (149), one has:

(150)
$$\dot{q}_{3i} = \frac{\dot{z}_i}{h} \qquad (z_i < h),$$

(151)
$$\dot{q}_{3i} = \dot{z}_i \qquad (z_i > h).$$

We next consider the first case. If one understands l_{3i} to mean the component of the energy of the ith molecule in the z-direction then, from (150), one has:

(152)
$$l_{3i} = \frac{h^2 m_i}{2} \dot{q}_{31}^{\ 2},$$

so, from (1):

$$p_{3i} = h^2\, m_i\, \dot{q}_{3i},$$

(153)
$$\dot{q}_{3i} = \frac{p_{3i}}{h^2 m_i}.$$

Thus, from (152), one has:

$$l_{3i} = \frac{p_{3i}^{\ 2}}{2h^2 m_i};$$

that is, from (148):

(154)
$$l_{3i} = \frac{p_{3i}^{\ 2}\, B^2}{2m_i a^2}.$$

By contrast, for:

$$z_i > h,$$

one will have:

$$p_{3i} = m_i\, \dot{q}_{3i},$$

(155)
$$l_{3i} = \tfrac{1}{2} m_i\, \dot{q}_{31}^{\ 2} = \tfrac{1}{2} m_i\, \frac{p_{3i}^{\ 2}}{m_i^2} = \tfrac{1}{2}\frac{p_{3i}^{\ 2}}{m_i}.$$

One will then have:

$$a\frac{\partial l_{3i}}{\partial a} = -\, 2\, l_{3i} \qquad (z_i < h),$$

$$a\frac{\partial l_{3i}}{\partial a} = 0 \qquad (z_i < h).$$

From (145), one will then have:

$$a\frac{\partial s}{\partial a} = k\, a + \sum_i -2l_{3i},$$

in which only molecules that are found completely within the container will be considered. However, the larger the container is, the smaller will be the fraction of the molecules that are in interaction with the piston. We assume that the container is large

enough that we can neglect that fraction. The sum can then be extended over all molecules, and one can write:

$$a \frac{\partial s}{\partial a} = k\,a - \sum_{i=1}^{\mathfrak{n}} 2l_{3i} ,$$

if one understands $\mathfrak{n} = n / 3$ to mean that number of all molecules. By taking the mean, it will emerge from this that:

$$\overline{a \frac{\partial s}{\partial a}} = \overline{k\,a} + \sum_{i=1}^{\mathfrak{n}} \overline{-2l_{3i}} .$$

However, since the same component of kinetic energy is assigned to each degree of freedom, one will have:

(156) $$\sum \overline{l_{3i}} = \tfrac{1}{3} \sum_{i=1}^{\mathfrak{n}} l_i = \tfrac{1}{3} L,$$

in which the right-hand side means the total *vis viva* of the gas molecule. We then get:

$$\overline{a \frac{\partial s}{\partial a}} = \overline{k\,a} - \tfrac{2}{3} L ,$$

or, from (146):

(157) $$\frac{\mathfrak{t}}{2} = \overline{k\,a} - \tfrac{2}{3} L .$$

However, from (37), one has:

(158) $$L = \frac{n}{2} \mathfrak{t} .$$

Thus, one will have:

$$\overline{k\,a} = \mathfrak{t} \left(\frac{n}{3} + \frac{1}{2} \right),$$

or, since n is very large:

(159) $$\overline{k\,a} = \tfrac{1}{3} n\, \mathfrak{t},$$

so, from (158):

(160) $$\overline{k\,a} = \tfrac{2}{3} L.$$

Equation (159) and (160) will be referred to as the *equation of state*.

The piston, whose mass might be denoted by M, will also possess kinetic energy. From (144), its mean will be:

$$\frac{1}{2} \overline{\dot{a} \frac{\partial s}{\partial a}} = \frac{M}{2} \frac{1}{B^2} \overline{\dot{a}^2} ,$$

so, from (34), one must have:

$$= \frac{3}{2} \frac{k\,\overline{a}}{n} ,$$

and therefore:

$$(161) \qquad \frac{\overline{\dot{a}^2}}{\overline{a}} = \frac{3k\,B^2}{M\,n}.$$

Now, when we appeal to ordinary units, the right-hand side of this equation will be extremely small. For instance, if only gravity acts upon the piston then:

$$\frac{k}{M} = \frac{g}{B},$$

in which g means the acceleration of gravity, and one will have:

$$(162) \qquad \frac{\overline{\dot{a}^2}}{\overline{a}} = \frac{3g\,B}{n}$$

in that case. However, since one has, in general ([1]):

$$(163) \qquad \overline{u}^2 < \overline{u^2},$$

one will have:

$$\overline{\dot{a}}^2 \leq \frac{\overline{a}}{n}\,3\,g\,B,$$

$$\overline{\dot{a}} \leq \sqrt{\frac{3g\,B}{n}}\,\frac{\overline{a}}{\sqrt{\overline{a}}}.$$

If τ denotes the time it takes to traverse the ε^*-surface once then the differential quotient $\dot{a}$ will have the same sign only in a fraction $\delta\tau$ of τ. During that time, a will suffer a fluctuation Δa, for which one will have the relation:

$$(164) \qquad \frac{\Delta a}{\overline{a}} \leq \frac{1}{\sqrt{n}}\,\frac{\sqrt{3g\,B}}{\sqrt{\overline{a}}}\,\delta\tau.$$

Obviously, the quantity on the right-hand side is extremely small, so we would be justified in assuming that a experiences no noteworthy changes. Therefore, we can also drop the mean value symbol in (160) and write, more briefly:

([1]) In general, for n arbitrary quantities, one will have:

$$(u_1 + u_2 + \ldots + u_n)^2 < n\,(u_1^2 + u_2^2 + \cdots + u_n^2).$$

In order to prove that inequality, one develops the left-hand side according to the polynomial law and replaces each doubled product $2\,u_i\,u_k$ with the larger sum $u_i^2 + u_k^2$.

(165) $$k\,a = \tfrac{2}{3}L.$$

The energy generally also possesses a component that includes $\dot{a}$, but since it is equal to the nth part of the total kinetic energy, it can be neglected, and the energy can be regarded as a function of q, p, and a.

Now, when the force that acts upon the piston varies, from (165), a will also experience a change ([1]). One can generate such a change in force by organic agencies, but we would not like to draw that possibility into the realm of our argument ([2]). However, still other cases are conceivable: It is possible that the gas that we have considered is coupled to a mechanical system whose influence is quite predominant in the combined system. The complicated problem of treating a complex that is assembled in that way will simplify in this case by a kind of distribution of work. In a first examination, we can infer the values that certain coordinates will assume as functions of time from the initial states of the influencing system and the mechanism of the influenced one, and we can do that independently of which initial state the influenced system possesses ([3]). In the second case under consideration, the coordinates that were just determined will be treated as constants, and the motion of the influenced system will be treated by the principles of the first paragraph.

One can express that state of affairs by saying: Our system possesses coordinates that prove to be constant for thermal processes, but can be changed from the outside. One calls such coordinates *external coordinates* or *variable parameters* of the system. Thus, the volume a of a gas that is enclosed by a piston is an external coordinate.

We then now leave the way in which such a change is produced outside of view, and consider only the case in which the parameter a changes very slowly. We imagine, e.g., a gas and suppose that the pressure that is exerted upon it varies gradually. However, it is, in turn, necessary to assume that a potential energy exists between the piston and the molecule. In fact, under these circumstances, nothing stands in the way of enclosing the q in the domain of variation from $-\infty$ to $+\infty$, so the space that is available to q will not change with a.

§ 11. Adiabatic processes.

The considerations of the previous paragraph make it understandable how the concept of external coordinates can be combined with our foundations. We now set aside the specialization that we introduced and assume a system that possesses an external coordinate that varies by external agencies. We demand that the energy should be a function of q, p, and a:

(166) $$\varepsilon = \varepsilon(q, p, q),$$

and assume that in the example that was considered it would, in fact, be made plausible that:

([1]) In order to exhibit it, one will require the energy equation, in addition to (165).

([2]) **H. Hertz**, *Mechanik*, pp. 45.

([3]) If one, e.g., atmospheric pressure k acts upon the piston then the respective a can be determined from (165). The value of k depends upon the dynamics of the sea of air, so the particular initial state of the gases has an infinitely small reaction on it.

1. No couplings are prescribed between the q, p, and a (and also no condition equations).

2. The change in a is left to our whims.

3. The change in the q and p takes place according to equations (2) and (3).

If we let a be constant then we will have a mechanism of the kind that we considered in the first part of our investigation. The changes in the q and p can be anticipated when one knows a, as long as ε is given as a function of the q and p. If a is varied then a new functional dependency will appear between ε and q and p. We can say: We go to a new mechanism. We are then dealing with changes in the mechanism in the second part. In that regard, it hardly needs to be remarked that the concept of mechanism possesses only a relative meaning. If one regards a as a variable in the same way then one will be dealing with a new state manifold for the same mechanism. However, it is convenient to appeal to the terminology that was just introduced.

An autonomous system always takes on new phases, but it will constantly keep the same ε. ε can be changed by thermal effects, but $\varepsilon\,(q,\,p)$ will still remain the same function. A third kind of process is characterized by saying that the functional dependency between ε and p and q changes in such a way that the mechanism will be altered. We must turn to the second part for that.

Thus, the mechanism shall be varied – i.e., an external coordinate a. We ask what variation of V is linked to it. That quantity must be changed for two reasons:

1. From (166), another ε will belong to the same q and p for a new choice of a. After a new choice of a, a phase for which ε was previously less than ε^{*} can continue to satisfy that condition, and conversely. Therefore, the same ε^{*} will correspond to another V with a new choice of a.

2. The change in a is generally impossible, unless ε^{*} itself is also given a new value. If we consider a change on these two grounds then we will write:

(167) $$V = V\,(a,\,\varepsilon^{*}),$$

(168) $$\frac{dV}{da} = \frac{\partial V}{\partial a} + \frac{\partial V}{\partial \varepsilon^{*}}\frac{\partial \varepsilon^{*}}{\partial a}.$$
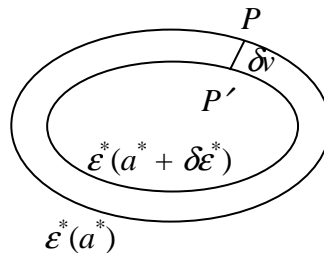
We next seek to determine $\partial V / \partial a$.

Figure 5.

With the original value a^* of a, there will be a well-defined ε^*-surface in whose interior all phases for which $\varepsilon < \varepsilon^*$ will lie. Another ε^*-surface will belong to the new value of a that might lie, e.g., inside the first one (Fig. 5). If we understand δv to mean the distance between them then:

(169) $$\delta V = - \int do\, \delta v.$$

How big is δv then?

Let P' mean a point on the surface $\varepsilon^*(a^* + \delta a^*)$, and let P be the point on the surface $\varepsilon^*(a)$ that lies opposite to it. If $a = a^* + \delta a^*$ then the ε that belongs to P' will be equal to ε^*, by construction, so when the parameter $a = a^*$, one will have, from (166):

$$\varepsilon^* - \frac{\partial \varepsilon}{\partial v} \delta \varepsilon^*.$$

On the other hand, for $a = a^*$, the ε that corresponds to P' must likewise be equal to ε^*, by construction, so for $a = a^*$, $\varepsilon_{P'}$ will also be given by:

$$\varepsilon^* - \frac{\partial \varepsilon}{\partial v} \delta v.$$

It follows from this that:

(170) $$\delta v = \frac{\partial \varepsilon / \partial a}{\partial \varepsilon / \partial v} \delta a^*,$$

so, from (169):

$$\frac{\partial V}{\partial a} = - \int do\, \frac{\partial \varepsilon / \partial a}{\partial \varepsilon / \partial v},$$

or, from (18) and (19):

(171) $$\frac{\partial V}{\partial a} = - \frac{\partial V}{\partial \varepsilon^*} \frac{\overline{\partial \varepsilon}}{\partial a}.$$

Secondly, the differential quotient $\partial \varepsilon^* / \partial a$ will be calculated. We then give a small increment δa to a and ask what the associated change $\delta \varepsilon^*$ in ε^* would be. We think of the variation δa as being broken into very many starting points that each bring about a change of $\eth a$. Each change $\eth a$ might last for a time interval that is small in comparison to the period of the system on the ε^*-surface; on the other hand, the intervals between the individual changes $\eth a$ might be very large in comparison to the period. The q and p will not change essentially during a process $\eth a$; however, from (166), the energy ε will probably experience an increment of $\eth a \cdot \partial \varepsilon^* / \partial a$, and transport the system to a higher ε^*-surface. In total, the increment δa will be linked with a change in energy of $\sum \eth a \cdot \dfrac{\partial \varepsilon}{\partial a}$.

Here, one must understand that the arguments of the function are the phases over all possible energy surfaces. However, infinitely-small, second-order errors will be introduced when each phase is replaced with the one on the original ε^*-surface that corresponds to it. Since the time interval between the individual $\eth a$ is large in

comparison to the period, all possible phases in the surface $\varepsilon = \varepsilon^*$ will occur as arguments $\partial \varepsilon / \partial a$, and each of them according to its frequency in the total time. One can then set:

$$\delta \varepsilon^* = \sum \overline{\frac{\partial \varepsilon}{\partial a}} \, \partial a \,,$$

but that is:

$$\delta \varepsilon^* = \overline{\frac{\partial \varepsilon}{\partial a}} \, \delta a$$

or ([1]):

(172)
$$\frac{\partial \varepsilon^*}{\partial a} = \overline{\frac{\partial \varepsilon}{\partial a}}.$$

Moreover, it follows from (168) and (170):

(173)
$$\frac{dV}{da} = 0.$$

It is then impossible to arrive at other values of V by changing only the mechanism.

For this analysis, it was essential to assume that the domain of variation of the q and p is also the same for a varying path; i.e., that no couplings exist between the a, q, and p. If such a coupling were present then it could happen that the surface that runs at a distance of $\delta v = \dfrac{\partial \varepsilon}{\partial a} \bigg/ \dfrac{\partial \varepsilon}{\partial v}$ inside of $\varepsilon = \varepsilon^*$ contains phases that are no longer admissible for $a = a^*$ + δa^*. One also now sees how it is necessary to consider the potential energy between molecules and the wall whenever one is given a molecular system that includes a wall. For example, in the case of ideal gases, one can introduce **Cartesian** coordinates if they are not considered. A drop in the piston would then leave the ε^*-surface essentially unchanged, except that only a very small fraction of it would cease to be admissible. One would then have $\partial V / \partial a = 0$, which would not be compatible with (173) and (168), since, from experiment, $\partial \varepsilon^* / \partial a \neq 0$. The contradiction is resolved as long as one assumes a potential energy that also becomes infinite for a finite penetration. Moreover, the differential quotient $\partial \varepsilon / \partial v$ that appears in (170) will become infinite at some places. One would do best in that case to appeal to the generalized coordinates that were introduced in the preceding paragraphs.

The changes that we are concerned with here, like the ones that were considered in § 8, will be induced by the influencing system. Thus, our entire approach to the proof will be based upon equation (166) essentially. That will demand that the energy of the influencing system can be determined from q, p, and a with no hindsight of the past (cf., pp. 7). Now, the external coordinates a of the influenced system are connected with certain external coordinates of the influencing system, and thus, a change in the mechanism of the influenced system, a change in the mechanism of the influenced system, and thus, with a change in the energy components that are assigned to the observable coordinates in the influencing system, with mechanical work. On the other

---

([1]) For the complete analysis, cf., **J. W. Gibbs**, pp. 153 (158), *et seq.*

hand, no energy can be transferred in the manner that was depicted in § 8 during the process, since otherwise equation (166) would not be valid. Physically, that means that the external system loses no heat energy, but only mechanical energy, or that no heat is introduced immediately into the system in question. Such processes are called *adiabatic*, and one can thus express (173) as: The quantity V remains constant under adiabatic processes.

§ 12. Reversible processes.

According to **Einstein** ([1]), the general thermo-mechanical process is composed of an isopycnic one and an adiabatic one. The increase $d\varepsilon^*$ of the energy will be equal to the sum of the thermal energy dQ that is given by external systems and the mechanical energy $-dA$ that they contribute. Therefore:

$$d\varepsilon^* = dQ - dA$$

or

(174)
$$dQ = d\varepsilon^* + dA.$$

Now, one will have the equations:

(155)
$$\frac{dQ}{t} = d \ln V,$$

(176)
$$\int \frac{dQ}{t} = \ln V + \text{const.}$$

In the first case, $dQ = 0$, and that will contain our statement in (173). In the second case, $dA = 0$, and our assertion will be a consequence of (174) and (144) ([2]). Thus, if the general mechanical-thermal process can be composed of adiabatic and isopycnic ones then one will generally have:

(177)
$$\int \frac{dQ}{t} = \int \frac{d\varepsilon^* + dA}{t} = S + \text{const.}$$

(178)
$$S = \ln V \, ([3]).$$

The quantity $S = \ln V$ can then be referred to as *entropy*.

Due to the invertibility of the mechanical equations, the adiabatic influence of a system must prove to be reversible. From (173), the entropy will be preserved by it. An isopycnic change of state will then be reversible when the influencing system possesses almost the same temperature as the influenced one. From (177), the total entropy will not be changed by such a process. One can then deduce: In a closed system the entropy is conserved by reversible processes.

([1]) **A. Einstein**, I, pp. 429, *et seq.*; II, pp. 178, *et seq.*
([2]) **A. Einstein**, II, pp. 180.
([3]) **J. W. Gibbs**, formula 485.

§ 13. Irreversible processes.

Let two systems Σ_1 and Σ_2 be given with different temperatures t_1' and t_2', resp., whose energies ε_1', ε_2', resp., belong to functions V_1' and V_2', resp. One can then find a pair of values ε_1'', ε_2'' that are different from ε_1', ε_2', resp., for which one has:

$$(179) \qquad \varepsilon_1'' + \varepsilon_2'' = \varepsilon_1' + \varepsilon_2',$$

$$(180) \qquad t_1(\varepsilon_1'') = t_2(\varepsilon_2'').$$

From (61), (63), (65), among all of the pairs of values that satisfy (179), the pair ε_1'', ε_2'' will give $V_1(\varepsilon_1) V_2(\varepsilon_2)$ its greatest value. Thus:

$$(181) \qquad V_1(\varepsilon_1'')V_2(\varepsilon_2'') > V_1(\varepsilon_1')V_2(\varepsilon_2').$$

However, from what we said in § 5 and (180), the bodies will take on the energies ε_1'' and ε_2'' after the resulting contact. Thus, if S' denotes the total entropy before the contact and S'', the total entropy after it then, due to (181) and (178), one will have:

$$(182) \qquad S'' > S'.$$

Contact between two bodies of different temperatures will lead to an increase in the entropy.

However, it follows from this that such processes are irreversible, and since they alone among the purely thermal processes are irreversible, we can further state: Entropy increases for irreversible thermal processes ([1]).

If we employ the fact that, the state of the system-pair will be more probable after contact in the proof then we will have introduced no new mechanical axiom, but merely inferred a consequence from the concept of probability. The physical assumptions that were used up to now were based upon only the fact that all phases in the ε^*-surface would always be traversed again. However, the fact that the system-pair will be found with greatest probability in the most probable phase by a sudden break at a random point in time follows from an axiom that precedes any mechanics, and belongs to merely the theory of probability itself. Thus, one cannot speak of a continuous change in the quantity $S = \ln V$. That function is not defined at all, in a certain sense, for a well-defined time point, but only for a time interval in which the ε^*-surface can be traversed several times. A new ε^*-surface will be traversed by a circulation after contact, and $\ln V_1 + \ln V_2$ will have a value that is larger than before by a finite amount.

([1]) Despite the invertibility of all mechanical processes, it is no contradiction to speak of irreversibility in a mechanical theory. When two systems that were previously separate are combined, one will artificially generate a lower value on the curve $V_1(\varepsilon - \alpha) V_2(\alpha)$, which can hardly ever be separated in the natural course of two permanently-coupled systems. Cf., **J. W. Gibbs**, pp. 150 (153). **P.** and **T. Ehrenfest**, *Mathematisch-naturwissenschaftl. Blätter*, no. 11 and 12, 1906; Phys. Zeit. (1907), 311, *et seq.*

In order to make the concept of probability more precise, we can also think of a virtual ensemble of $\mathfrak{N}$ system-pairs. They might possess all possible positions on the curve $f(\alpha)$ before contact. After contact, and the resulting separation, the majority of them will be found on the summit of the curve $f(\alpha)$. In other words: The phase that is most probable in the temporal ensemble of the individual system-pairs will be assumed by the majority of them. However, not only does each *phase* of the system-pair possess a probability inside of its temporal ensemble, but the *distribution* of the $\mathfrak{N}$ system-pairs over the phases will possess one, as well. Thus, the concept of probability will be regarded in a well-defined sense that was first given by **Boltzmann** and applied in a completely different way from what we did here. When one, like **Einstein** ([1]), assumes that more probable distributions will follow more improbable ones, one will thus introduce a special assumption that is based upon no sort of evidence and is not at all required by the proof. Such an assumption was generally made by **Gibbs** ([2]), and seems to me to be applicable, despite the objections that were raised against it ([3]).

Whereas the representation of entropy that was chosen here would change discontinuously under the separation, the **Gibbs** theory led to a continuous change in entropy. The fact that the concept of virtual ensembles is physically justified was shown in § 5. By contrast, the definition of entropy that is based upon them is linked with another difficulty. In order to verify the characteristic property [formula (177)] of the expression for entropy that is presented in that way, one must define the temperature to be the modulus of a canonical ensemble. However, such a definition does not need to possess any physical meaning. Therefore, it seems to me, at least up to now, that the definition of entropy that was given here, which likewise goes back to **Gibbs** and deviates from the **Einstein** definition only inessentially, is preferable.

Heidelberg, 24 May.

(Received on 25 May 1910).

—————

([1]) **A. Einstein**, II, pp. 184. In addition, the use of the canonical ensemble complicates the physical interpretation. The theory of probability was used in a different sense – namely, the one here – in a second derivation by **Einstein**, III, pp. 326.

([2]) **J. W. Gibbs**, pp. 150 (pp. 153).

([3]) **E. Zermelo**, Jahresberichte der deutschen Mathematiker-Vereinigung **15** (1906), pp. 238. **T** and **P. Ehrenfest**, Wiener Ber. **115** (1906).