Examination of the foundations of thermodynamics

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Introduction

Among the most noteworthy advances in the research of the last century into thermodynamics, one must indeed include the discovery that this discipline is free of any basic hypothesis that cannot be experimentally verified. The standpoint that most of the authors in the last fifty years have taken since the great discoveries of R. Mayer, the measurements of Joule, and the ground-breaking work of Clausius and W. Thomson, is perhaps the following one:

There is a physical quantity, which is not identical with the mechanical quantities (mass, force, pressure, etc.), whose changes can be determined by calorimetric measurements, and which one calls *heat*. Heat has the property of being comparable to ordinary mechanical work under certain circumstances, but beyond that, when two bodies with differing temperatures come into contact it always flows from the hotter one to the colder one, and never the converse.

Now, although no other assumptions on the nature of heat can be made, one can construct a theory that accounts for all of the results of experience. The understanding of this theory will later be made easier by the introduction of a new notion, whose importance in all of physics had gradually emerged, that of *energy*. This physical quantity has the property of depending only upon the instantaneous state of the various substances considered, which is not true of heat.

The first main theorem of heat theory amounts to a *definition of energy* and states that this quantity can be determined in any concrete case with the help of mechanical and calorimetric measurements.

However, various authors have already remarked that this point of view contains an over-determinacy: [*]) *One can derive the entire theory without assuming the existence of a physical quantity that deviates from ordinary mechanical quantities, namely, heat.*

The purpose of the present work is to show this as clearly as possible in all of its details. Naturally, one can develop a physical theory in very different ways. I have chosen an arrangement of the conclusions that differs from the classical proofs as little as possible and likewise exhibits the parallelism that must necessarily exist between the main results of the theory and the picture that emerges from the measurements that are actually carried out.

The essential feature of the presentation that is given here consists in the fact that the notions of "adiabatic" and "adiabatically isolated" do not lead back to that of energy, as they usually are, but are defined through physical properties. One can then express the axiom of the first law in such a way that it corresponds to the experimental set-up of Joule precisely when one regards the calorimeter that is used in it as an adiabatically isolated system.

For the axiom of the second law I have chosen a definition that is very applicable to that of Planck, but the latter must be modified in a certain way, in order to take into account the fact that heat and quantity of heat are not defined anywhere in our manner of representation.

I have thoroughly examined the conditions under which an adiabatic change of state is reversible, or furthermore, a system of sufficient conditions under which this is the case. I then came to the definition of certain thermodynamic systems that one can call "simple," because they can be treated precisely like the simplest systems that are known to thermodynamics. This terminology deviates from the one that Bryan introduced in his aforementioned Encyklopädie article. [**])

Finally, in order to be able to treat systems with arbitrarily many degrees of freedom from the outset, instead of the Carnot cycle that is almost always used, but is intuitive and easy to control only for systems with two degrees of freedom, one must employ a theorem from the theory of Pfaffian differential equations, for which a simple proof is given in the fourth section.

At the conclusion, I would like to draw attention to the fact that the notion of temperature is not included in the coordinates from the outset, but first appears as a result of certain equations of condition, which are presented on pp. 16. The grounds for which

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[*]) Encyklopädie der mathem. Wiss. v. 3, Bryan, Thermodynamik, pp. 81. J. Perrin, Le contenu essentiel des principes de la thermodynamique. Bull. de la soc. franc. de philos., t. VI, 1906, pp. 81.

[**]) loc. cit., pp. 80.

this conception of temperature is to be preferred are briefly hinted at in the final section; they originate in certain situations that give rise to radiative phenomena.

1. **Definitions**

In the following investigation, we will deal with the description of the thermal properties of systems that exist in various chemical substances.

However, the general principles from which this description can be attained come to light in their full generality when we, in order to make things more concise, specialize the problem and make the same assumptions as – say – Gibbs did in the first part of his ground-breaking treatise "On the equilibrium of heterogeneous substances." [*])

At the end of this work, we will suggest how one can also treat further questions with these same principles.

With the aforementioned authors, we would also like to postulate [**]) that when the system S is found in equilibrium a finite number α of fluid or gaseous media are present – the "phases"

$$\varphi_1, \varphi_2, \ldots, \varphi_\alpha$$

of the system – and that external forces, such as gravity, as well as electromagnetism and capillarity, are to be neglected. [***])

The system S that we consider will now be *defined* by associating it with certain "symbols," the totality of which will completely characterize the system.

To that end, we consider any equilibrium point of S and direct our attention to its phases:

$$\varphi_1, \varphi_2, \ldots, \varphi_\alpha$$

in sequence. We associate each of these phases φ_i with two types of symbols: First, certain *features* by which the chemical composition of φ_i will be established qualitatively, such that the various substances and compounds that appear in φ_i will be enumerated. Second, *numbers* that one obtains by *measurements*. These numbers represent the following quantities:

    a) The total volume V_i of the phase φ_i.
    b) The pressure p_i that the phase in question exerts on the bodies that it contacts.
    c) The set:

$$m_{1i}, m_{2i}, \ldots, m_{\beta i}$$

of different substances and compounds that exist in any unit volume of φ_i.

If the first phase exists as, e.g., a solution of salt in water then for our theory a particular equilibrium point of this phase would be characterized completely by the numbers V_1, p_1, and a symbolic equation such as:

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[*]) J. W. Gibbs: Scientific Papers, vol. I, pp. 55.
[**]) Loc. cit., pp. 62.
[***]) The consequences of the latter two assumptions first appear in the second section.

(1) $\varphi_1 = m_{11}H_2O + m_{21} \text{ NaCl}.$

All of the phases φ_i will now indeed be uniquely characterized through symbolic equations such as (1) and the totality of numbers:

(2) V_i , p_i , $m_{\chi i}$ $i = 1, 2, \cdots, \alpha$
                                                                $\chi = 1, 2, \cdots, \beta$

although, by comparison, the entire system S will not, by any means. To that end, we must consider the properties of S that come about from the contact between the different phases or the walls of the vessels that contain them, resp.

Therefore, we assume that the mass of these walls is so small that our later results will not be restricted by the fact that we have not included the walls themselves in the phases φ_i . For a general theory in which fixed isotropic and crystalline bodies can appear in the phases, these restrictions will disappear.

The physical properties of the walls of the vessels that contain one or more phases are now of a very diverse nature.

Such a vessel Γ can have the property that, e.g., the phases that are found in its interior remain in equilibrium and the numbers (2) that represent these phases preserve their values when one alters the bodies that are found in the exterior of the vessel with only the single restricting condition that Γ shall remain at rest and preserve its original form; a "Thermos bottle" is a tangible example of such a vessel. I would, however, like to expressly emphasize that the wall of Γ does not need to be rigid, and one may indeed think in terms of a completely deformable vessel Γ that possesses the aforementioned properties. The changes in the bodies that are found external to Γ must then be restricted in such a way that the pressures that they exert on Γ do not deform it.

A vessel with these properties imposed on it shall be called *adiabatic*, and the phases that it contains are *adiabatically isolated.*

If two phases φ_1 and φ_2 meet along a rigid adiabatic wall then, by analogy with the foregoing, no equation of condition will exist between V_1, p_1, $m_{\chi 1}$ and V_2, p_2 , $m_{\chi 2}$ due to this contact; two arbitrary equilibrium points for the phases of S that are found on both sides of the wall can, in other words, coexist.

For other rigid bodies, however, it can happen that the equilibrium can exist only when one or more relations of the form:

(3) $F(V_1, p_1, m_{\chi 1}; V_2, p_2, m_{\chi 2}) = 0$

are fulfilled. One then says that the wall is "permeable." A wall can be either permeable only "to heat" or also for some of the chemical substances that contact it, as well, or it exhibits complicated behavior. What each of these various expressions means must be *defined* precisely each time one *experimentally* establishes the equations of conditions in the form (3) that describe the thermodynamical properties of the wall in question. For a non-rigid wall, one must add the condition that the pressure on both of its sides must be the same.

There likewise exist necessary conditions of the form (3) for equilibrium when no material wall is found between the phases φ_1 and φ_2 and these phases come into direct contact.

The exploration of all such conditions, to the extent that they appear in nature, defines one of the main problems of thermodynamical measurements, and we will further focus our attention on the most important of them.

For the time being, however, it suffices for us to know that when one (in order to simplify the notation) denotes the sequence of numbers (2) collectively by:

(4) $$c_0 , c_1 , c_2 , \ldots, c_{n+\lambda}$$

certainly mutually independent equations:

(5)
$$F_1(c_0,c_1,\cdots,c_{n+\lambda}) = 0,$$
$$F_2(c_0,c_1,\cdots,c_{n+\lambda}) = 0,$$
$$\ldots$$
$$F_\lambda(c_0,c_1,\cdots,c_{n+\lambda}) = 0,$$

between these numbers must necessarily be satisfied in order for equilibrium to exist.

We now make the assumption that we can experimentally determine *all* equations of condition of this type; i.e., that for each combination of numbers (4) that satisfy equations (5) an equilibrium point can be established that corresponds to these numbers. Experience suggests that this assumption will be satisfied in each concrete case.

Definition I. *Two systems S and S′ shall be called "equivalent" when there exists a one-to-one correspondence between their phases, in the sense of equation* (1)*, and moreover when the corresponding coefficients c_i , c_i' must be subject to the same or mathematically equivalent conditions* (5) *in order for equilibrium to be possible.*

In the sequel, equivalent systems shall not be distinguished. The "symbols" that *define* our system *S* are thus, on the one hand, symbolic equations like (1), and, on the other, the system of equations (5).

We now add to system (5) $(n + 1)$ equations of the form:

(6)
$$G_1(c_0,c_1,\cdots,c_{n+\lambda}) = x_0,$$
$$G_2(c_0,c_1,\cdots,c_{n+\lambda}) = x_1,$$
$$\ldots$$
$$G_\lambda(c_0,c_1,\cdots,c_{n+\lambda}) = x_n.$$

The functions G_i shall be chosen in such a way that when one varies the c_i in them between the bounds imposed in practice, and likewise considers the conditions (5) then a *one-to-one* correspondence exists between the possible systems of values for:

$$c_0 , c_1 , \ldots, c_{n+\lambda}$$

and the corresponding one for:
$$x_0 , x_1 , \ldots, x_n .$$

Therefore, it is necessary (but not sufficient) that the functional determinant:

$$\frac{\partial(G_0, G_1, \cdots, G_n; F_1, F_2, \cdots, F_\lambda)}{\partial(c_0, c_1, \cdots, c_{n+\lambda})}$$

for all of the values of c_i that come into consideration be different from zero. [*]) Thus, one can solve the system of equations (5), (6) for the c_i here, and consider the c_i to be functions:

(7) $c_i = c_i(x_0, x_1 , \ldots, x_n),$

that satisfy the system of equations identically when they are substituted.

Through a one-to-one correspondence between the various possible equilibrium points of S and the system of values of the sequence of numbers:

(8) $x_0, x_1 , \ldots, x_n ,$

we have achieved the means to compare these equilibrium points with each other and to represent them by "general coordinates" that are analogous to the ones that are used in mechanics.

Any system of numbers (8) corresponds, as one says, to a "state" of the system S, and for the numbers x_i themselves we would like to introduce the name of "*state coordinates.*"

In order to use the language of geometry in the following, it is convenient to regard the state coordinates as Cartesian coordinates in $(n+1)$-dimensional space; each state of S then corresponds to one point of this multidimensional space, and the totality of the equilibrium points that come into consideration is then mapped onto a certain region G of this space.

One then has the following theorem that summarizes the above:

Definition II: *In order to characterize the equilibrium points of a system, the state coordinates* (8) *come into consideration exclusively, and two equivalent systems for which these quantities agree shall be identical objects from the thermodynamical standpoint.*

We now consider "changes of state" of the systems, i.e., transitions of one equilibrium point into another. Changes of state will be characterized by certain symbols precisely as the equilibrium points are.

The coordinates of the initial state and final state are to be regarded in this way. Furthermore, another quantity comes into consideration that is associated with each

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[*]) The non-vanishing of the functional determinant has only the one consequence, namely, that there is a one-to-one correspondence between c and x "in the small;" i.e., it exists in the neighborhood of any individual point However, this does not state that the neighborhood of x is not multiply covered.

change of state, and which one calls the *external work*; this quantity, which we denote by *A*, shall originate in the systems that are considered here exclusively from the deformations of the *external* form of *S*. [*]) They shall be identical with the mechanical work that any force delivers when it is exerted by any bodies that lie on the exterior of *S* (but contact the system) during the change of state considered. The physical meaning of these forces is clear, and one can also measure *A* at any time by means of certain mechanical devices, such as one employs in technology for testing steam and gas motors.

Finally, however, we associate the change of state with a special feature. Namely, when the system *A* is adiabatically isolated during the entire time interval of a change of state one calls that change of state itself *adiabatic*; the adiabatic changes of state shall define a particular class.

We thus arrive at the following definition:

Definition III: *Each change of state will be characterized by the coordinates of the initial state and the final state, the external force that is applied to them, and the given of whether they are adiabatic or not.*

2. **Axioms**

Certain *axioms* are valid for the notions that were described in the foregoing sections, i.e., generalizations of the facts of experience that will be observed under certain particularly simple circumstances. Thermodynamics knows two mutually independent axioms of this type:

The first one defines the foundations of the so-called "first law" of heat theory, and is nothing but an expression for the general energy principle for the system considered by us.

We would like to give it the following statement:

Any phase φ_i of a system S is, in equilibrium, associated with a function ε_i of the quantities (2):

$$V_i, p_i , m_{\chi i} ,$$

which is proportional to the total volume of this phase and is called the internal energy of this phase.

The sum:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_\alpha ,$$

when taken over the totality of the phases, is called the internal energy of the system.

Under any adiabatic change of state, the external work done A by the change in energy is equal to zero; hence, in symbols, when one denotes the initial and final energy by e and $\bar{\varepsilon}$:

(9) $$\bar{\varepsilon} - \varepsilon + A = 0.$$

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[*]) This follows from the fact that we neglect the distant forces.

The formulation of the first law that was given just now includes the assumptions that were made at the beginning of this work, that neither distant not capillary forces shall be considered. Namely, had, e.g., capillary forces been considered then one would have to say that the sum over the various volume energies of the phases no longer represents the total energy ε of S, and that one must add certain terms to this sum that arise from the separating surface between the phases. Moreover, if distant forces between the phases were noteworthy then new terms would likewise enter in that arise from the interaction between the phases, not from one phase alone, and would be dependent upon several of them.

The second law that now comes into question is of a completely different nature: Namely, one has found that under all adiabatic changes of state that start from any given initial state certain final states are not attainable and that such "unattainable" final states can be found in any neighborhood of the initial state.

However, since physical measurements cannot be absolutely precise this fact of experience includes more than the mathematical content of the aforementioned law, and we must demand that when a point is excluded, the same shall also be true of a small region around this point whose size depends upon the precision of the measurement. However, in order for us to give this precision no weight it is convenient to give the axiom in question a somewhat more general form, and indeed in the following way:

Axiom II: *In any arbitrary neighborhood of an arbitrarily given initial point there is a state that cannot be arbitrarily approximated by adiabatic changes of state.*

3. **Simple systems**

The problem of the further examination, with the help of the two main axioms, now consists in explaining the possibility of the experimental determination of the internal energy of each of the physical systems examined, and likewise finding out the general properties of the energy function ε.

We will see that these problems are relatively easy to solve for certain special systems, which we would like to call "simple systems." Now consider a given phase φ_1, whose internal energy one would like to describe as comprising a component of one such simple system, and if one knows, from prior examination, the internal energy of the remaining phases then one has all of the data that one needs; from axiom I, one then has the equation:

$$\varepsilon_1 = \varepsilon - \varepsilon_2 - \varepsilon_3 - \ldots - \varepsilon_\alpha.$$

The problem of constructing the "simple" system that corresponds to a given phase in each case that occurs in practice is one of the most important ones, but also one of the hardest, of thermodynamic measurement; the physical chemists call it "making a reversible process." For our general investigation, however, this problem itself does not enter into the considerations; it suffices for us to know that it is to be dealt with in general.

The properties that characterize "simple systems" are of a diverse nature.

First, all of the state coordinates of *S* *except for one* shall depend upon only the external form of the system. We would like to call these coordinates that establish the external form *deformation coordinates;* upon consideration of eq. (5), they must include only the quantities V_1, V_2, …, V_α.

This is found to be the case, for example, when the system exists in a single phase in which all of the state quantities except for the pressure *p* and the total volume *V* are constant, or also when *S* exists in two such phases that are separated by a rigid wall that is permeable "only for heat." Then in this case the external form of *S* depends upon two quantities, namely, the total volumes V_1 and V_2 of its two components, and the system has two deformation coordinates, whereas between the four quantities V_1, p_1, V_2, p_2 that come into consideration here, one relation:

$$F(V_1, p_1, V_2, p_2) = 0$$

must exist due to the permeability of the wall (cf. § 6), such that *S* ultimately possesses only three state coordinates.

From this first property of simple systems it follows that when one knows the initial point of an adiabatic change of state, from the final form of the system and the external work done during the change of state, the final state of the simple system *S* can be calculated with the help of equation (9):

(9) $$\bar{\varepsilon} - \varepsilon + A = 0$$

(assuming that the energy ε is also known as a function of the state coordinates, and, as we likewise will see, is still not determined from the form of the system).

A second assumption that shall be valid for simple systems is that the external work that is done during an adiabatic change of state shall not be uniquely determined in terms of the initial and final states alone. On the contrary, adiabatic changes of state shall be possible that lead from a given initial state to the same prescribed final state and which correspond to different amounts of work done. When, e.g., a gas is found in an adiabatic cylinder that is closed off by a moving piston then the work that is done by the piston under a prescribed expansion of the gas varies with the velocity by which one withdraws the piston.

This assumption has the consequence, when one considers equation (9), that the energy ε, when regarded as a function of the coordinates x_i, includes that coordinate that does not depend upon the external form of *S*. Let x_0 be this coordinate, and, by contrast, let x_1, x_2, ., …, x_n be the coordinates of the deformation of the system.

We would now like to consider the various values of *A* that are possible when the system goes from a prescribed initial state to a prescribed final state. One can interpret the totality of all these values as a point set on a line. As a third property of simple systems, we would like to assume that in each possible case this point set is always *connected*. In other words, it shall fill out a single interval that usually can be extended to infinity in both directions.

From this last property, it follows, with the help of equation (9), that the possible values for x_0 under the same circumstances also define a connected point set, at least

when the domain of variation of the state coordinates is restricted to a certain neighborhood of the initial point.

Leaving from a given initial point, one can obviously actually arrive at any possible final form under the influence of particular external forces. However, one can do more: Namely, the change of form of the system S that takes place during an adiabatic change of state is a prescribed function of time. In other words: one can prescribe n functions

$$(10) \qquad\qquad x_1(t), x_2(t), \ldots, x_n(t)$$

and demand that the change of state that goes through them is of a sort that the timelike variation of the coordinates $x_1, x_2, \ldots, x_n$ will be represented by the sequence (10). This new description of a change of state, under which only the variation of x_0 is left out of consideration, is much more comprehensive than the one that we considered earlier; we would like to leave open the question of how an adiabatic change of state can be found that makes the magnitude of the corresponding external work A uniquely determined by the initial state and the functions (10) alone. On the contrary, when the velocity with which the system is deformed becomes "infinitely slow," or, more precisely, when the derivatives:

$$x_1'(t), x_2'(t), \cdots, x_n'(t)$$

converge uniformly to null, the work A shall go to a definite value in the limit. We would like to call a change of state that takes place so slowly that the difference between the applied external work and this limiting value falls beneath the observed limit a *quasi-static* change of state.

If, under a quasi-static change of state, the external work is known as a function of time then one can, with the help of the equation:

$$\mathcal{E}\{x_0, x_1(t), x_2(t), \ldots, x_n(t)\} - \mathcal{E}_0 + A(t) = 0,$$

in which $\mathcal{E}_0$ means the initial value of the energy, then one can also regard the remaining coordinate x_0 as also being a definite function of t. A quasi-static, adiabatic change of state can thus be interpreted as a *sequence of equilibrium points*, and each quasi-static, adiabatic change of state corresponds to a certain curve in the space of x_i.

Finally, we would like to make one last assumption: Under any quasi-static change of state one shall be able to measure the external work A as if the forces that bring about this work were the same as the ones that are necessary to maintain equilibrium when, in the foregoing, one regards the change of state as a sequence of equilibrium points. These latter forces are, however, functions of only the states.

Therefore, the expression for A must necessarily have the form:

$$(11) \qquad\qquad A(t) = \int_{t_0}^{t} DA,$$

in which DA represents a Pfaffian expression:

$$(12) \qquad\qquad DA = p_1\, dx_1 + p_2\, dx_2 + \ldots + p_n\, dx_n,$$

and the $p_1, \ldots, p_n$ mean functions of the $x_0, x_1, \ldots, x_n$.

The functions p_i can be determined experimentally when, for each state of S, one measures the forces that must act on the system from the outside in order for equilibrium to exist. As long one is dealing with quasi-static adiabatic changes of state, one can now give equation (9) of the first law the form:

$$(13) \qquad \int_{t_0}^{t_1} [d\varepsilon + DA] = 0,$$

and since this relation must be valid for each t the conclusion follows that absolutely no curve in the $(n+1)$-dimensional space of the x_i for which the Pfaffian equation:

$$(14) \qquad d\varepsilon + DA = 0$$

is satisfied can represent a quasi-static, adiabatic change of state.

Conversely, however, any curve in the $(n+1)$-dimensional space of the x_i that satisfies equation (14) can be regarded as the trace of a quasi-static, adiabatic change of state in our simple system.

In fact, let such a curve segment be given in parametric representation through the equations:

$$(15) \qquad \begin{cases} x_0 = x_0(\tau), x_1 = x_1(\tau), \cdots, x_n = x_n(\tau), \\ \qquad\qquad 0 \leq \tau \leq 1. \end{cases}$$

If one now sets:

$$\tau = \lambda t,$$

in which t means time and λ, a parameter, then one can introduce adiabatic changes of state that satisfy the equations:

$$x_1 = x_1(\lambda t), \qquad x_2 = x_2(\lambda t), \ldots, x_n = x_n(\lambda t),$$

for each prescribed value of λ. For a sufficiently small λ, a change of state of this sort is now quasi-static and must ultimately satisfy equation (14). By integrating this equation, however, one finds that:

$$x_0 = x_1(\lambda t),$$

which proves our assertion.

Had we now substituted:

$$t = 1 - \lambda t$$

in equation (15), then for increasing t and sufficiently small λ, precisely the same curve would have been traversed, but in the opposite sense.

Quasi-static, adiabatic changes of state of a simple system are "reversible."

In the usual representation of the theory, one introduces "reversible" changes of state as something that is given intuitively; however, when one looks closer, the properties that one associates with reversible processes are precisely the ones that we based our definition of simple systems upon. We summarize this as follows:

Definition. *A "simple" system with the (n+1) state coordinates must satisfy the following conditions:*

1. *n of its coordinates – e.g., x_1, x_2, …, x_n – are deformation coordinates.*

2. *The external work A is not uniquely determined by the initial state and final state of S under adiabatic changes of state. The totality of all these possible values for A under these assumptions defines a connected set of numbers.*

3. *Under "quasi-static" adiabatic changes of state the external work is equal to an integral of a definite Pfaffian expression of the form:*

$$DA = p_1\, dx_1 + p_2\, dx_2 + \ldots + p_n\, dx_n\,.$$

Ordinarily, one assumes that the first assumption on the number of deformation coordinates entails the other two. The examples that we gave on page 8 would then be simple systems. This assumption, which we will always make from now on, is permissible for the substances that one examines in general, and especially for gases and fluids; after learning the consequences that we shall now deduce, it then agrees quite well with the results of measurement.

On the other hand, it is quite conceivable, and also physically conceivable, that substances can be present in nature that one can never regard as the components of simple systems. This would be the case, e.g., when the internal friction of the substance in question, which is generally a function of the deformation velocity, does not converge to zero under quasi-static changes of state. The forces that produce the external work A would then no longer be comparable to the equilibrium forces; the external force A itself could not be represented with the help of a Pfaffian expression such as (12), and the quasi-static changes of state would ultimately not be reversible. Our theory, with nothing further, does not allow itself to carry over to the sort of systems that usually must likewise be the case in classical thermodynamics.

The application of the axioms of the two laws to quasi-static, adiabatic changes of state in simple systems will now allow us to normalize the state coordinates of these systems in a characteristic way; for this, however, we need a mathematical theorem on Pfaffian equations, which we would now like to derive.

4. **Lemma from the theory of Pfaffian equations.**

If a Pfaffian equation:

(16) $$dx_0 + X_1\, dx_1 + X_2\, dx_2 + \ldots + X_n\, dx_n = 0$$

is given, in which the X_i are finite, continuous, differentiable functions of the x_i, and one knows that in any neighborhood of an arbitrary point P of the space of x_i there is a point that one cannot reach along a curve that satisfies this equation then the expression (16) *must necessarily possess a multiplier that makes it into a complete differential.*

Let:

$$a_0\,,\ a_1\,,\ \ldots,\ a_n$$

be the coordinates of P. There are then, by assumption, infinitely many points P_i that have the point P for an accumulation point and possess the property that no single curve exists that satisfies the differential equation (16) that includes both P and the P_i .

However, since the coefficient of dx_0 does not vanish, one can always find curves C_i that satisfy equation (16), include P_i , and lie in the two-dimensional plane that connects P_i with the line G:

$$x = t, \quad x_k = a_k \hspace{4cm} (k = 1, 2, \ldots, n),$$

in the event that P_i does not itself already lie on this line. Let Q_i be the point of intersection of C_i with G; by their construction, the points Q_i must converge to P for increasing i. The points Q_i can also be reached by curves that start at P and satisfy equation (16), since one would then, by the addition of the curve C_i , also reach P_i , contrary to the assumption. From this, it follows that in any interval on the line G that includes P there must be points that cannot be reached by starting from P.

One now considers a line G_1, which is parallel to G, but otherwise arbitrary, and an arbitrary two-dimensional cylinder that connects G_1 to G. Let M be the point where any curve that satisfies equation (16), lies on this cylinder, and includes P, intersects the line G_1 . Under an arbitrary variation of the cylinder the point M must remain fixed; in the opposite case, any curve of the differential equation (16) that lies on the varied cylinder that goes through M can include an arbitrary point in the neighborhood of P on the line G. In this way, we can thus reach certain points Q_i along curves of the differential equation (16) that go from P to M, which was excluded.

If one now continuously varies the position of the lines G_1 then M would describe an n-dimensional surface, and all of the curves of the differential equation (16) that go through P must lie on this surface. The point P was, however, chosen arbitrarily; by varying its position one thus obtains a family of surfaces:

$$F(x_0 , x_1 , \ldots, x_n) = C$$

that depends upon the parameter C and on which *all of the* curves of the differential equation (16) must lie. The coefficients of the dx_i in the two equations:

$$dx_0 + X_1 \, dx_1 + X_2 \, dx_2 + \ldots + + X_n \, dx_n = 0,$$

$$\frac{\partial F}{\partial x_0} dx_0 + \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 + \cdots + \frac{\partial F}{\partial x_n} dx_n = 0$$

are thus proportional to each other, and one has the equation:

$$dF = \frac{\partial F}{\partial x_0}\{dx_0 + X_1 dx_1 + X_2 dx_2 + \cdots + X_n dx_n\}$$

(17)

$$\frac{\partial F}{\partial x_0} \neq 0, \quad \frac{\partial F}{\partial x_0} \neq \infty,$$

from which, our theorem is proved.

5. **Normalization of the coordinates of a simple system**

Let S be a simple system, which may depend on the coordinates:

(18) $$\xi_0 \, , \, x_1 \, , \, x_2 \, , \, \ldots, \, x_n \, ,$$

in which the last n quantities in the sequence (18) represent deformation coordinates, and the external work for quasi-static changes of state is produced by an integral of the expression:

$$DA = p_1 \, dx_1 + p_2 \, dx_2 + \ldots + p_n \, dx_n \, .$$

The adiabatic, quasi-static changes of state of the system can be represented by the curves of the Pfaffian equation:

(19)
$$d\varepsilon + DA = \frac{\partial \varepsilon}{\partial \xi_0} d\xi_0 + X_1 dx_1 + X_2 dx_2 + \cdots + X_n dx_n = 0,$$

$$X_i = \frac{\partial \varepsilon}{\partial x_i} + p_i.$$

If one could reach each point of a certain neighborhood of this initial location along curves of the differential equation (19) that start from a give initial point then one could also, from our assumptions on the simple systems, approximate any arbitrary final state by adiabatic changes of state. From our axiom II, however, the latter shall be impossible. On the other hand, due to the properties of simple systems, $\partial \varepsilon / \partial \xi_0$ is not identically null; one could then, when one omits certain singular places, divide the expression (16) by $\partial \varepsilon / \partial \xi_0$ and arrive at precisely the same conclusions as in the foregoing section.

The expression (19) thus possesses a multiplier that is neither null nor infinite. If one denotes it by $1/M$ then one ultimately has:

(20) $$d\varepsilon + DA = M \, dx_0 \, ,$$

in which x_0 means a certain function of the variables (18). However, one now has, by comparing (19) and (20):

$$\frac{\partial x_0}{\partial \xi_0} = \frac{\dfrac{\partial \varepsilon}{\partial \xi_0}}{M} ;$$

hence, from the above, it is different from zero. One can therefore solve the equation:

$$x_0 = x_0(\xi_0 \, , \, x_1, \, \ldots, \, x_n)$$

for ξ_0, and introduce x_0 as the $(n+1)^{\text{th}}$ coordinate of our system in place of ξ_0, along with the n deformation coordinates.

If we do this then the expression:

(21) $$DA = p_1 \, dx_1 + p_2 \, dx_2 + \ldots + p_n \, dx_n$$

for the external work takes on its original form, because it does not include the differential $d\xi_0$; now, however, the p_i are functions of the new variables x_0 , x_1, …, x_n . Likewise, the function M in (20) must be regarded as dependent upon these same variables.

The curves that correspond to adiabatic, quasi-static changes of state in our system now satisfy the equation:

(22) $$x_0 = \text{const.}$$

Conversely, any curve in the space of the x_i that leaves x_0 constant can be regarded as the trace of a change of state of that sort; namely, equation (22) is equivalent to (19), and we have seen in the third section that curves that satisfy this equation possess the desired property.

One now remarks that equation (20) is an identity, and if one replaces the expression (21) for DA in this equation then one finally obtains the relations:

(23) $$M \, dx_0 = d\varepsilon + DA = \frac{\partial \varepsilon}{\partial x_0} \, dx_0 ,$$

(24) $$p_i = -\frac{\partial \varepsilon}{\partial x_i} \qquad\qquad i = 1, 2, \ldots, n.$$

A coordinate system that possesses all of the properties cited in (21), (23), (24) shall, in the following, be called a "normalized" coordinate system. Therefore, it must be remarked that these properties all remain valid when one replaces x_0 with an arbitrary function $f(x_0)$ of these quantities, which usually follows directly from the theory of multipliers for a Pfaffian expression.

In thermodynamics one can distinguish a certain normalized coordinate system among all of the possible ones that is uniquely determined and, with the help of the physical properties of rigid bodies, will be defined only for heat-permeable walls; this shall be our next problem.

6. **Conditions for thermal equilibrium**

Let two simple systems S_1 and S_2 be given with the normalized coordinates:

$$x_0 , x_1 , \ldots, x_n ,$$
$$y_0 , y_1 , \ldots, y_n .$$

These systems shall be separated by a fixed wall that is permeable only by heat. Such a wall will be defined by the following properties:

1. The deformation coordinates of the two systems in question can be varied independently of each other after the introduction of a coupling.

2. After any arbitrary change of form of the total system, when it is adiabatically isolated, equilibrium is reached after a finite time.

3. The total system S is then only found, but also always therefore in equilibrium, when a certain relation between the coordinates x_i, y_i of the form:

(25) $$F(x_0, x_1, \ldots, x_n; y_0, y_1, \ldots, y_m) = 0$$

is satisfied.

4. Whenever any two systems S_1 and S_2 are in equilibrium with a third system S_3 under analogous conditions, there likewise exists equilibrium between S_1 and S_2.

This latter condition therefore means the same thing as saying that for the three equations:

(26)
$$F(x_0, x_1, \cdots, x_n; y_0, y_1, \cdots, y_m) = 0,$$
$$G(x_0, x_1, \cdots, x_n; z_0, z_1, \cdots, z_k) = 0,$$
$$H(y_0, y_1, \cdots, y_m; z_0, z_1, \cdots, z_k) = 0,$$

which, analogous to (25), bring about equilibrium between S_1 and S_2, S_1 and S_3, S_1 and S_3, each of them is a consequence of the other two.

This is, however possible only when the system of equations (26) is equivalent to a system of the form:

$$\rho(x_0, x_1, \ldots, x_n) = \sigma(y_0, y_1, \ldots, y_m) = \tau(z_0, z_1, \ldots, z_k).$$

In particular, the condition (25) can then be replaced by two equations of the form:

(27)
$$\rho(x_0, x_1, \cdots, x_n) = \tau,$$
$$\sigma(y_0, y_1, \cdots, y_m) = \tau,$$

in which τ means a new variable.

One calls this quantity τ the *temperature* and equations (27) the *equations of state* of the systems S_1 and S_2.

On the other hand, the system (27) is, however, equivalent to a system of the form:

$$W\{\rho\} = \tau_1, \quad W[\sigma] = \tau_1,$$

where W means an arbitrary function. The functions (27) are therefore not uniquely determined; one expresses this indeterminacy by saying that the "temperature scale" can be chosen arbitrarily.

From our assumptions, one further deduces that at least one of the quantities $\partial\rho / \partial x_0$, $\partial\sigma / \partial y_0$ is not identically null. Namely, if these two quantities were null then ρ and σ would depend only upon x_0, x_1, $\ldots$, x_n; y_0, y_1, $\ldots$, y_m. However, they are nothing but deformation coordinates that one can vary independently of each other; one would thus be able to reach states for which it would be impossible to satisfy the equation (25), which contradicts our two assumptions on thermal equilibrium.

One of these quantities – e.g., $\partial\rho / \partial x_0$ – is therefore different from zero, and one can, at points in general position, express x_0 as a function of the remaining $(n+m+1)$ coordinates with the help of the equation:

$$\rho = \sigma.$$

The system S can thus be considered to be a system with $(n+m+1)$ degrees of freedom that possesses $(n+m)$ deformation coordinates. From our assumption on page 12, it is therefore a simple system to which our prior results can be applied.

7. **Absolute temperature**

The assumption that is appropriate to the foregoing sections is that the energy ε of our total system S is equal to the sum of the energies ε_1 and ε_2 of its two components. Likewise, the external work A that is done on S during an arbitrary change of state is equal to the sum of the quantities A_1 and A_2 that are associated with the two systems S_1 and S_2. However, these latter systems were simple and their coordinates were normalized. Therefore, one can write:

$$d\varepsilon_1 + DA_1 = M(x_0 , x_1 , ..., x_n)\, dx_0 ,$$
$$d\varepsilon_2 + DA_2 = N(x_0 , x_1 , ..., x_n)\, dx_0 .$$

By adding these equations one obtains:

(28) $d\varepsilon + DA = M\, dx_0 + N\, dy_0 .$

However, the system S is also a simple system, as we have proved. Therefore, upon consideration of (27) the expression on the right-hand side of (28) must possess a multiplier.

We would now like to assume that in nature at least one system exists whose equation of state includes one more deformation coordinates. Experience teaches that this assumption is satisfied for, e.g., gases. If we now choose such a system for S_1 then it follows that the function ρ includes at least one of the quantities $x_1 , ..., x_n$ – say, x_1 . We can then regard the quantity M in (28) as a function of:

$$x_0 , \ \tau, x_1 , ..., x_n \ .$$
For the equation of state:
$$\sigma(y_0 , y_1 , ..., y_m) = \tau,$$

we now focus our attention upon all of the possibilities.

1. In the case where σ depends upon no single one of the quantities $y_0 , y_1 , ..., y_m$, the τ in M must be replaced with a particular value. In the identity that now exists:

(29) $du = \lambda[M\, dx_0 + N\, dy_0]$

the function u must depend upon only x_0 and y_0, such that λM and λN also depend upon only these two variables. Now, since the y_i do not appear in M, λ cannot include any of the deformation coordinates of S_2 ; however, they do not enter into λM, either. It follows that N is also free from these quantities and depends upon just y_0 .

2. In the case where σ depends upon only the one state coordinate y_0 , one would replace the quantity τ in M with a function of y_0, and in the same way deduce the conclusion that N also includes only y_0 here.

The fact that neither of these two cases occur in nature is in no way a contradiction to our assumptions about simple systems.

3. Finally, we consider the case in which at least one deformation coordinate also enters into σ. Let it be – say – y_1; we can now regard this latter quantity, and as a result, also the quantity N, as functions of:

$$y_0 , \ \tau, \ y_2 , y_3 , \ …, y_m .$$

In (29), λM and λN are also now functions of only x_0 and y_0 . Now, since M, as well as λM, do not include the coordinates $y_2 , y_3 , …, y_m$, the same is true for λ. It follows that N is also independent of these quantities since otherwise λN would also include these quantities.

From the analogous considerations for the x_i , one finally derives the result that λ depends upon at most x_0 , y , τ, while M depends upon only x_0 and τ, and N depends upon only y_0 and τ .

Now, since λM and λN are also independent of τ , one thus has:

$$M \frac{\partial \lambda}{\partial \tau} + \lambda \frac{\partial M}{\partial \tau} = 0, \qquad N \frac{\partial \lambda}{\partial \tau} + \lambda \frac{\partial N}{\partial \tau} = 0,$$

from which one concludes that the logarithmic derivative:

$$\frac{1}{\lambda} \frac{\partial \lambda}{\partial \tau}$$

of λ with respect to τ can depend upon neither y_0 not x_0, and it follows that λ decomposes into a product of the single variable τ and a function of x_0 and y_0 . Therefore, one write:

$$\lambda = \frac{\psi(x_0, y_0)}{f(\tau)} ,$$

and from this it further follows, since λM is a function of x_0 and y_0 alone, that M must have the form:

$$M = f(\tau)\, \alpha(x_0),$$

and in precisely the same way, one sees that:

$$N = f(\tau)\, \beta(y_0).$$

The most general splitting of M and N into a product of two factors, one of which depends upon only τ and the other, upon only x_0 (y_0, resp.), when C means an arbitrary non-null constant, is:

(30)
$$M = Cf(\tau)\frac{\alpha(x_0)}{C}, \qquad N = Cf(\tau)\frac{\beta(y_0)}{C}.$$

If one starts with a given temperature scale then for any system whose equation of state includes one of the deformation coordinates the function $f(\tau)$ is completely determined up to a multiplicative constant, and the same is true for all such systems.

If one now remarks that such a splitting of the function N is possible for the systems that we examined in 1 and 2 then we see that the function $f(\tau)$ possesses a completely general physical meaning. The temperature scale that is defined by this function:

$$t = Cf(\tau)$$

will be called *absolute.* In order to also determine the constants, one also prescribes the difference of two fixed temperatures – e.g., the melting of iron and the evaporation of water – under prescribed pressures.

8. **Entropy**

For any simple system, one can, from (23) and (30), normalize the coordinates such that one can have:

$$DA = -\frac{\partial \varepsilon}{\partial x_1}dx_1 - \frac{\partial \varepsilon}{\partial x_2}dx_2 - \cdots - \frac{\partial \varepsilon}{\partial x_n}dx_n,$$

$$\frac{\partial \varepsilon}{\partial x_0} = \frac{t\alpha(x_0)}{c},$$

in which t means the absolute temperature. We now introduce a new coordinate η with the help of the equation:

(31)
$$\eta - \eta_0 = \int_{a_0}^{x_0} \frac{\alpha(x_0)}{c}dx_0 \; ;$$

equation (31) can be solved for x_0 since M, and therefore, from (30), also α, is non-zero. The total differential of the energy function now assumes the form:

(32)
$$d\varepsilon = t\, d\eta - DA.$$

This new coordinate η was called the *entropy* of the system by Clausius, and is determined up to an arbitrary additive constant by (31).

For the system $S = S_1 + S_2$ that we considered in the previous section, one has, for any quasi-static change of state, when η_1, η_2 mean the entropies of S_1 and S_2 :

$$d\varepsilon = d\varepsilon_1 + d\varepsilon_2 = t(d\eta_1 + d\eta_2) - DA_1 - DA_2 .$$

Thus, when η_1 and η_2 are expressed with the help of the equations:

(33)
$$\eta_1 + \eta_2 = \eta,$$
$$\frac{\partial \varepsilon_1}{\partial \eta_1} - \frac{\partial \varepsilon_2}{\partial \eta_2} = 0,$$

as functions of x_i, y_k and the new η variables, the total differential of the total energy ε once again takes on the form (32). The entropy of the total system is therefore equal to the sum of the entropies of its various components. Many physicists have overlooked this additive property of entropy, which also persists when one considers other walls besides planes that are permeable by only heat and are put between the systems S_1 and S_2, as one can gather from the theory of these walls, in order to regard entropy as a physical quantity that is similar to the mass that is attached to any spatially extended body, although it is dependent upon the instantaneous state of that body.

Since, from (30), the entropy depends only upon x_0 in normalized coordinates, it remains constant for any quasi-static, adiabatic process, and any change of state of a simple system under which the entropy remains constant is, from our prior argument, *reversible*.

9. **Irreversible changes of state**

We have assumed that under adiabatic changes of state that are caused by the possible values of the work done for a given initial and final form, simple systems define a connected numerical set. If one now calculates the corresponding final values of the entropy η with the help of the formula:

$$\varepsilon(\eta, x_1, x_2, ..., x_n) - \varepsilon_0 + A = 0,$$

which is valid for *arbitrary* adiabatic processes, then it follows from continuity considerations that they also fill up an entire interval. The initial value η_0 of the entropy must necessarily be a point of this interval; the value of η then remains unchanged under quasi-static changes of state, which can indeed also be counted among the ones that come under consideration. Now, if η_0 were an *interior* point of the interval then one could next assume that under adiabatic changes of state the value of η would be arbitrary in a certain neighborhood of η_0, and then under quasi-static changes of state for a fixed η the deformation coordinates would change arbitrarily. However, this contradicts the axiom of the second law.

The value η_0 is thus found at an *endpoint* of the interval in question. From this, it follows that under arbitrary adiabatic changes of state that start from a given initial state the value of the entropy can be neither increase nor decrease.

If one varies the initial state then one sees that, due to continuity, the impossibility of an increase or decrease in entropy for two arbitrary initial states of the same system must always follow in the same way. The same is also true, however, of two different systems S_1 and S_2, due to the additive property of entropy that we spoke of in the preceding paragraphs.

Whether the entropy can only increase or only decrease depends upon the constant C in formula (31), in which η enters multiplicatively. One chooses these constants in such a way that the absolute temperature t is positive. Experiences then teaches that one only needs a single experiment to confirm that *entropy never decreases.*

From this, it follows that equilibrium will always come about when the entropy must decrease under all permissible virtual changes of state of a simple system, and it then possesses a maximum in the equilibrium state.

In addition, however, it follows from our conclusions that if the value of the entropy does not remain constant under any change of state then no adiabatic change of state can be found that takes the system in question from its final state to its initial state.

Any change of state under which the value of entropy changes is "irreversible."

10. **Possibility of the experimental determination of energy, entropy, and absolute temperature**

We must show that the quantities ε, η, and t that we introduced into our considerations can be determined by experiment in any concrete case. The simplest way that this is achieved is when one, as we would now like to do, assumes that one can observe reversible processes with sufficient accuracy. Since nothing stands in the way of this assumption from a logical standpoint, one comes to the insight that thermodynamics is purely experimental; i.e., can be founded without any assumption on the nature of "heat."

In reality, one would encounter difficulties in the application of the method that was given here that arise from the unavoidable errors in observation. One thus divides the problem into two pieces: First, one determines the absolute temperature scale; I will not go into this question in the present work, since it requires lengthy discussion. However, if t is known then one can compute the quantities ε and η rather easily, as we will see in the following sections, and indeed computations in which one employs measurements that can be made very accurately.

Here, we assume that a simple system S is given that may depend upon the coordinates:

$$\xi_0 , x_1 , x_2 , \ldots, x_n ,$$

in which the x_i mean the deformation coordinates. Furthermore, the following functions shall be capable of being established by measurements:

1. The equation of state of S for any temperature scale τ.

(34) $$\psi(\xi_0 , x_1 , x_2 , \ldots, x_n) = \tau .$$

2. The coefficients of the Pfaffian expression for the work A:

(35) $$DA = p_1 \, dx_1 + p_2 \, dx_2 + \ldots + p_n \, dx_n \, .$$

3. The coefficients of the Pfaffian equation for quasi-static, adiabatic changes of state:

(36) $$0 = \frac{1}{\dfrac{\partial \varepsilon}{\partial x_0}} (d\varepsilon + DA) = d\xi_0 + X_1 \, dx_1 + X_2 \, dx_2 + \ldots + X_n \, dx_n \, .$$

In order to experimentally determine the coefficients X_1, X_2, …, X_n in this latter expression one makes the following attempt: One considers adiabatic changes of state of the system under which only one deformation coordinate – e.g., x_1 – increases by Δx_1, while x_2 , x_3 , …, x_n remain constant. One measures the change $\Delta \xi_0$ in ξ_0 that comes about during this process. When Δx_1 is sufficiently small and, in addition, the change of state results sufficiently slowly, one then has:

$$X_1 = - \frac{\Delta \xi_0}{\Delta x_1}$$

for the initial state in question.

The Pfaffian expression (36) must, from the previous results, possess a multiplier λ that makes it into a complete differential when the quantities X_i satisfy certain differential equations that must necessarily exist for any actual system as long as our theory is correct.

There then exists the equation:

$$\lambda(d\xi_0 + X_1 \, dx_1 + X_2 \, dx_2 + \ldots + X_n \, dx_n) = dx_0 \, ,$$

which one can integrate. If one now chooses x_0 to be any of its integrals then that quantity can be introduced as a new coordinate. Therefore, from (34), one will have:

(37) $$\varphi(x_0 , x_1, \ldots, x_n) = \tau,$$

and (35) also preserves its original form, except that the p_i must be regarded as functions of the new variables.

If we now make the Ansatz for the absolute temperature t:

$$t = \beta(\tau)$$

then it follows from equations (24) and (32) that:

(38) $$d\varepsilon = \beta(\tau) \, \alpha(x_0) \, dx_0 - p_1 \, dx_1 - \ldots - p_n \, dx_n \, .$$

The functions α and β must be determined in such a way that the expression (38) is integrable.

This is first possible only when (35) is also integrable for constant x_0, from which certain conditions for the p_i arise that must be satisfied for any system. If we further set:

$$x_2 = a_2 , \; x_3 = a_3 , \; \ldots, \; x_n = a_n ,$$

where the a_i refer to constants, and introduce the relations:

(39) $\tau = \varphi(x_0 , x_1, a_2, \ldots, a_n) = f(x_0 , x_1),$
(40) $p_1(x_0 , x_1, a_2, \ldots, a_n) = g(x_0 , x_1),$

then the expression:

$$\beta(f(x_0 , x_1)) \, a(x0) \, dx_0 - g(x_0 , x_1) \, dx_1$$

must be an exact differential, which yields the condition:

$$\beta'[f(x_0,x_1)]\frac{\partial f}{\partial x_1}\alpha(x_0)+\frac{\partial g}{\partial x_0}= 0$$

or:

(41) $$\beta'(\tau) \, \alpha(x_0) = - \; \dfrac{\dfrac{\partial g}{\partial x_0}}{\dfrac{\partial f}{\partial x_1}} .$$

The right-hand side of this equation must then, if one introduces x_1 as a function of x_0 and τ into it with the help of (39), split into a product of a function of x_0 and a function of τ, such that one can write:

$$- \dfrac{\dfrac{\partial g}{\partial x_0}}{\dfrac{\partial f}{\partial x_1}} = \Psi(x_0) \, \Theta(\tau).$$

If C and C' are yet-to-be-determined constants then one finally obtains:

$$t = \beta(\tau) = C\int_{\tau_1}^{\tau} \Theta(\tau)\,d\tau + C' ,$$

$$\alpha(x_0) = \frac{1}{C} \, \Psi(x_0).$$

The first of these equations represents the absolute temperature, while the second one allows one to determine the entropy:

$$\eta - \eta_0 = \frac{1}{C} \int_{a_0}^{x_0} \Psi(x_0)\,dx_0 .$$

One obtains the integration constant C, when one prescribes the difference D in absolute temperature between two given temperatures τ_1 and τ_2 arbitrarily, from the formula:

$$C = \frac{D}{\int_{\tau_1}^{\tau_2} \Theta(\tau)\,d\tau}.$$

By the introduction of the values found for α and β into (38) one can integrate these equations when the integrability conditions are all satisfied, as must be true in concrete cases, and obtain:

$$\varepsilon - \varepsilon_0 = C'(\eta - \eta_0) + F(\eta, x_1, \dots, x_n).$$

One sees that during reversible processes one can determine the absolute temperature only up to an additive constant and the internal energy only up to a linear function of the entropy.

However, one can remove this indeterminacy when one observes C' for all time with the help of a single *irreversible* adiabatic process; e.g., one in which no external work is done. In this case, the energy remains constant, while the coordinates experience measurable changes, from which a linear equation for C' arises.

For ideal gases, the calculations take on the following form: When, for constant total mass, we choose the coordinates to be the pressure p and the specific volume v, we have the equation of state:

$$pv = \tau$$

and the equation of the adiabatic curves:

$$pv^{\gamma+1} = \text{const.}$$

We can thus set:

$$v = x_1, \qquad pv^{\gamma+1} = x_0$$

and obtain, for formulas (39) and (40):

$$\tau = f(x_0, x_1) = x_0 x_1^{-\gamma},$$
$$p = g(x_0, x_1) = x_0 x_1^{-(\gamma+1)}.$$

Here, equation (41) takes the form:

$$\beta'(\tau)\alpha(x_0) = \frac{1}{\gamma x_0},$$

such that one obtains:

$$t = \beta(\tau) = Ct + C', \qquad \alpha(x_0) = \frac{1}{C\gamma x_0},$$

$$d\varepsilon = \left[\frac{x_1^{-\gamma}}{\gamma} + \frac{C'}{C\gamma x_0}\right] dx_0 - x_0 x_1^{-(\gamma+1)} dx_1.$$

The integration of the latter equation now yields:

$$\varepsilon - \varepsilon_0 = \frac{x_0 x_1^{-\gamma}}{\gamma} + \frac{C'}{C\gamma} \log x_0 ,$$

or, when we once again introduce τ and v as coordinates:

$$\varepsilon - \varepsilon_0 = \frac{\tau}{\gamma} + \frac{C'}{C\gamma} l\tau + \frac{C'}{C} lv .$$

One now needs an irreversible process in order to determine the value of C'. Under adiabatic expansion, during which no work is done on the gas, τ, for example, remains constant. One thus has $C' = 0$, and the well-known formulas:

$$\varepsilon = \frac{1}{C\gamma} t , \qquad pv = \frac{1}{C} t ,$$

which easily lead back to the usual relations.

11. **Practical determination of ε and η**

In this section, we assume that the absolute temperature is known already and that for a simple system S, whose state coordinates may again be:

$$\xi_0 , x_1 , x_2 , \ldots, x_n$$

one can measure the following data:
1. The equation of state:
2. The functions $p_1 , p_2 , \ldots, p_n$ in the Pfaffian expression for the external work.
3. The "specific heat" for constant volume. The latter means that with the help of calorimetric measurements – i.e., by observing certain irreversible processes – the quantities:

$$\frac{\partial \varepsilon}{\partial t}$$

can be obtained for constant $x_1 , x_2 , \ldots, x_n$.

From 1, it follows that one can choose the $(n+1)$ independent coordinates to be:

$$t, x_1, x_2 , \ldots, x_n ,$$

in which t again represents the absolute temperature. In these coordinates, (32) has the form:

$$d\varepsilon = t \frac{\partial \eta}{\partial t} dt + \sum_{1}^{n} \left[t \frac{\partial \eta}{\partial x_i} - p_i \right] dx_i .$$

Since this expression shall be a complete differential, one has, due to the integrability conditions:

(42) $$\frac{\partial \eta}{\partial x_i} = \frac{\partial p_i}{\partial t} \qquad\qquad i = 1, 2, \ldots, n.$$

In addition, however, from 3, we know the quantities:

(43) $$\frac{\partial \eta}{\partial t} = \frac{1}{t}\frac{\partial \varepsilon}{\partial t}.$$

Equations (42) and (43) allow the entropy η to be determined uniquely, up to an additive constant, when only certain integrability conditions between the p_i and the $\partial \varepsilon / \partial t$ are satisfied. If one introduces the value (42) into $d\varepsilon$ then one obtains the equation:

(44) $$d\varepsilon = t\frac{\partial \eta}{\partial t}dt + \sum_{1}^{n}\left[t\frac{\partial p_i}{\partial t} - p_i\right]dx_i,$$

which can be integrated as long as the conditions above are satisfied.

By integrating equations (42), (43), and (44), one thus obtains all of the data that one needs.

One would be led to precisely analogous calculation if one had measured the specific heat for constant external forces instead of the specific heat for constant volume. However, one does not first compute the energy ε, but the "thermodynamic potential:"

$$\varepsilon - p_1\,dx_1 - p_2\,dx_2 - \ldots - p_n\,dx_n\,.$$

12. **Crystalline media**

All of our procedures and results up to now can be carried over to the general case where some of the media are fixed and possess a crystalline structure.

The only difference is that the quantities that characterize these phases are different from the ones that were considered heretofore. Along with the volume V, differential invariants that were defined in elasticity theory come into consideration here. Since we assume that the individual phases are homogeneous these quantities are the same at any point of a phase and can be regarded as characteristic features of the entire phase.

Instead of pressure, which is no longer independent of direction here, one must introduce the "mechanical invariants;" i.e., the coefficients of the differentials of the deformation quantities in the Pfaffian expression for the external work, which will likewise be drawn from the theory of elasticity.

When one further adds the quantity V, these collectively constitute thirteen coordinates, in place of the two – viz., V and p – that we had up to now. This number can, however, be reduced for special crystalline systems.

By comparison, the chemical coordinates – i.e, the quantities $m_{\chi i}$ – that we considered in the first section of this work are precisely the same as before.

Between these various quantities, however, certain relations exist, also when we consider the individual phases, while previous equations of condition can only apply when the various phases come into contact. For the statement of these relations, I must again refer to the theory of elasticity.

13. **Remarks on the consequences of the thermodynamical theorems**

The manner in which we have derived the main results of thermodynamics, and particularly the way that we presented the notion of "absolute temperature" and "entropy," allows us to suspect (since other ways of presenting the theory are conceivable) that these theorems and notions are linked to many assumptions and their domain of validity is correspondingly restricted.

Naturally, certain generalizations are possible that are achieved with no further assumptions. One can thus immediately free oneself from the assumption that the various media shall be homogeneous. One thus needs only to regard the state coordinates that we had up to now as functions of position and to modify the definition of the internal energy and the work done from the outside with the help of particular corresponding integrals. The difficulties that arise from such generalizations are of a purely mathematical nature; they are easily treated separately and will in no way detract from out results.

Similarly, one can treat the case where capillary forces are considered. A thermodynamic treatment of this problem can be found in the aforementioned treatise of Gibbs and already seems to include all of our main ideas that might lead to completely satisfying solutions of these questions.

By comparison, the problems of radiation and "heat motion" lead to difficulties of a completely different nature; thus, in particular, so does the thermodynamics of moving media.

For the simplest radiative phenomena, in order to define equivalent systems or the state of a system one no longer begins with a finite number of coordinates. The emission capability of the substance, as well as its dispersion and absorption capabilities, must then be given for *every* wavelength, such that now not just *numbers* are necessary to describe these properties, but *functions* that depend upon one or more variables. The same distinction presents itself in mechanics when one goes from systems with a finite number of degrees of freedom to continuum mechanics.

Now, the notion of temperature is not a primary one; i.e., one must be able to present the various state coordinates without making use of this quantity. As we saw, temperature enters into the calculations when one considers certain equilibrium conditions. One can now seek to *define* the temperature of a radiative medium S_1 by the condition that it is in equilibrium with our previous system S_2, which possesses the temperature t. However, the fact that such a definition can lead to indeterminacy can be seen from the fact that the system S_2 must now likewise be regarded as a radiative medium. However, there can very well exist two systems S_2' and S_2'' that are different from each other from the viewpoint of radiation, whereas, for ordinary thermodynamics, which knows less state coordinates, they represent precisely the same situation. Thus, it does not need to be true that S_1 is likewise in equilibrium with S_2' and S_2'', and when this is the case this system cannot possibly possess a temperature in the ordinary sense of the

word. Before one responds to this question, it must be subjected to a thorough test. One can make completely similar thoughts valid for the notion of entropy, whose definition is so closely connected to that of absolute temperature.

In cases where the thermodynamics of moving media (among which one can also count the theory of heat conduction) can be treated without considering radiation phenomena the difficulties are of a different nature.

Here, one would probably associate each material point of the systems with a certain temperature that varies with time. This temperature can, however, possibly depend upon all of the state coordinates here, and thus also on the velocity.

Nevertheless, for the determination of the energy function and equations of motion our previous methods cannot be employed since all such processes are now always irreversible, due to the internal friction that one cannot neglect.

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