Tab. 1.

| Mittlere Temperatur in °C | $\sigma = D'/D \cdot 10^3$ | $D \cdot 10^5$ |
|---|---|---|
| 35,0 | 6,2 | 2,1 |
| 44,5 | 5,7 | 2,5 |
| 55,0 | 5,2 | 2,9 |

erwarten wäre. Prigogine[2] hat aus kinetischen Betrachtungen $D'/D$ als Funktion von Temperatur und Verdampfungswärmen der reinen Substanzen dargestellt. Diese Formel gibt allgemein das richtige Vorzeichen des Effekts, kann aber die absolute Größe nur ungefähr wiedergeben.

Bearman, Kirkwood und Fixman[3] haben aus statistischen Überlegungen $D'/D$ als Funktion von partieller Verdampfungswärme, Molvolumina und Selbstdiffusionskonstanten ermittelt. Jedoch bleibt in der Formel ein Paarpotential bestehen, was den Vergleich mit Experimenten nicht leicht durchführen läßt.

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# A Nonenergetic Theory of Heat

## A Suggestion for a New Concept of Thermodynamics

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The current interpretation of heat is completely different from the earlier concept which was quite successful at the beginning. Then, it was thought that heat was a quantity which could be neither created nor destroyed and that it was present in every material body. A body should become hotter by absorption of heat and expand, melt, vaporize or decompose, if the temperature necessary for these processes is reached[1–5]. On this basis, Black explained the existence of latent heats[3], Carnot calculated the effective work of ideal heat engines[4], Clapeyron found the connection between vapor pressure and heat of vaporization[6] and Thomsen developed the first material-independent definition of temperature[7]. In spite of their success, these interpretations were in opposition to several experimental results showing that heat was obviously produced by consumption of work. These facts indicated a relationship between the two quantities.

Clausius and Thomsen succeded simultaneously in explaining the experiments by developing their abstract theory assuming the equivalence of heat and work[8, 9]. This hypothesis, missing the simplicity and elegance of the older view[10], diplaced at first only slowly, but later completely, all other concepts[11] in explaining heat phenomena.

It is remarkable that it turns out now, that only small corrections of the old concept of heat would have been sufficient to remove the contradiction with experimental evidence. One only needs to replace the second sentence of this paper by: "Heat is an indestructible quantity present in all material bodies" and then, together with the energy principle in the form "work can be neither created nor annihilated" *, one gets an axiomatic system which can describe heat phenomena in an equally favourable manner as the two principles of Clausius. The theory developed from these two axioms keeps the intuitive clearness and terseness of the older theory of heat[12]. In this paper, the development of this theory from the basic hypothesis, as well as some special results will be briefly described. It will turn out that heat in this theory is entropy in the conventional sense.

From the assumption that heat can be created but not destroyed it can be deduced that it cannot be produced by reversible processes. If one wants to be sure that the quantity of heat will not change during measurement, one may demand the reversibility of all procedures. This is especially necessary for the transmission of heat to a calorimeter. In this case, conduction of heat in a temperature gradient must be excluded, but the use of a Carnot process is possible. If one observes these precautions, the heat can — as is usual — be measured calorimetrically or be defined by adequate instructions for measurement. If one wants to be in-

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[8] R. Clausius, Pogg. Ann. **79**, 368 [1850].

[9] E. Mach, Prinzipien der Wärmelehre, Verlag Ambr. Barth, Leipzig 1900.

[10] R. Clausius, Die Mechanische Wärmetheorie, Verlag Vieweg, Braunschweig 1887, S. 356 u. 361.

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* More exactly: work can neither be created nor annihilated without consuming or producing an equivalent (delay of a moving body, lowering of a weight, alteration of a charge distribution, consumption of fuel etc.).

[12] G. Job, Anschauliche Wärmelehre (yet unpublished).

dependent of a special temperature scale, ice calorimeters can be used, as was suggested and practised by some past and modern authors [13–15].

Temperature can be best defined as "heat potential" analoguous to THOMSEN's definition in 1848 [7]. According to this definition, the temperature difference $T'' - T'$ between two bodies ($''$) and ($'$) is given by the work $\mathrm{d}W$, necessary for the transport of a small heat quantity $\mathrm{d}S$ from ($'$) to ($''$)

$$T'' - T' = \mathrm{d}W/\mathrm{d}S\,.$$

The yield of work $W$ of a heat engine working between two heat reservoirs at constant temperature, directly results from the above definition

$$W = S(T'' - T') = S\,T'' - S\,T',$$

i. e. as the product of the transmitted quantity of heat $S$ and the "potential difference" $T'' - T'$ or from the difference of the "potential energy" of $S$ in both reservoirs. The quantity $T$ can — without contradiction — also be interpreted in the sense of the old views of LAMBERT [1], PICTET [16] and certainly, too, of CARNOT [17]. According to these authors, temperature can be thought of as a tension pressing upon the heat since it is the driving power of the heat flow. Against this tension, heat can be pressed into a body (i. e. the quantity $\mathrm{d}S$) only by consumption of work ($T\,\mathrm{d}S$).

The absolute value of the temperature of a body can be found if one determines the work $\mathrm{d}W_\mathrm{e}$ necessary for the production of a small measurable quantity $\mathrm{d}S_\mathrm{e}$. Owing to the energy principle, the potential energy $T\,\mathrm{d}W$ of the produced heat in the body has to be equal to the work spent:

$$\mathrm{d}W_\mathrm{e} = T\,\mathrm{d}S_\mathrm{e}\,,\ \text{and, therefore,}\ T = \mathrm{d}W_\mathrm{e}/\mathrm{d}S_\mathrm{e}\,.$$

If all heat is removed from a body, the temperature drops to absolute zero.

For all processes where energy is released, it can be collected as the "potential energy" of the produced heat $T\,S_\mathrm{e}$; therefore, $E_\mathrm{e} = T\,S_\mathrm{e}$. Beyond that, energy must be converted in this way if it cannot be consumed otherwise. For example, this is true for the conduction of electricity and also for the entirely analoguous process of the conduction of heat where, by transmission of the heat from a higher to a lower temperature, part of its potential energy is set free. As assumed, heat is indestructible and therefore such processes can only proceed in one direction and only as long as all energy surplus is consumed. A system remains in equilibrium if there is no possibility that energy will be set free and heat produced, respectively, for any virtual change of state.

This is the basis on which the conception of thermodynamics easily can be developed further, whereby that point can be reached where its structure is congruous to those already known from other branches of physics. Then, the dependence of the quantities can be understood directly and can also be illustrated by means of mechanical or electrical examples. Thus, to help describe the mutual dependence of the "work-coordinates" and "forces" of a thermodynamic system, the comparison with an elastic body can be used. By a formalism developed for this conception ("Stürzregel"), one obtains easily the already qualitatively predictable results in a quantitative form. Besides, this formalism can be favourably applied to conventional thermodynamics [18] using neither CARNOT cycles nor characteristic functions.

It is remarkable that by the same way of thinking and calculation, the dependence of those quantities can be easily understood which are connected by the principle of ONSAGER.

According to the suggestion made by THOMSEN with respect to the heat, potentials can be introduced in a similar way for the different substances. The difference of the "substance potential" of a substance contained in to bodies ($'$) and ($''$) can be given by

$$\mathrm{d}W/\mathrm{d}n = r'' - r'$$

where $\mathrm{d}W$ is the necessary work needed for the transfer of a small quantity of substance $\mathrm{d}n$ from ($'$) to ($''$), whereby certain precautions will have to be observed. As this is true in case of the temperature, the "substance potentials" can be interpreted as tensions being the driving forces for diffusion and flow processes, chemical reactions and phase transformations. As long as there are tension and potential differences, energy can be set free and heat can be produced, respectively, by substance transfer from places with higher $r$-values to lower ones. Substance potentials can be absolutely determined [19] under certain circumstances. In order to have the quantity $\mathrm{d}n_\mathrm{A}$ of a substance A pressed into a body, the work $r_\mathrm{A}\,\mathrm{d}n_\mathrm{A}$ against the existing tension $r_\mathrm{A}$ has to be done. In case of a mixed phase, whereby, besides volume and heat contents, the quantity of all components can be varied by exchange with the surroundings, the alteration of their energy $E$ is given by an expression which is analoguous to the fundamental equation of GIBBS, i. e. by the sum of the mechanical, thermal and chemical work:

$$\mathrm{d}E = -p\,\mathrm{d}V + T\,\mathrm{d}S + \sum r_i \cdot \mathrm{d}n_i\,.$$

A comparison with conventional thermodynamics shows that the heat $S$ can be identified with the entropy and the heat potential with the absolute thermodynamic temperature. Likewise, the substance potentials $r$ in bodies which are stationary and free from external fields are identical with the chemical potentials. Apart from the fact that many variables will no

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[18] G. JOB, Z. Naturforsch. **25 a**, 1502 [1970].

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longer be present in the new form, the type of the quantities has not changed substantially in spite of the different starting point. What has changed, however, is their conceptional arrangement.

The advantage of the new concept can be chiefly found in the fact that the abstractness and difficulty [20–22] of the energetic theory of heat and its extended formalism will disappear.

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# Viscosity of Ammonia and its Mixtures with Noble Gases in an Electric Field

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The component $\eta_3$ of the viscosity of ammonia increases in an electric field. The effect depends on $E^2/p$ and tends to a saturation value close to that found from measurements in a magnetic field. In ammonia-helium mixtures the saturation value of the effect decreases and becomes negative at an ammonia concentration of about 40%.

The viscosity of $NH_3$, $ND_3$ and mixtures of $NH_3$ with helium and argon have been measured in a static, homogeneous, external electric field with methods described elsewhere for other polar gases [1–3]. Ammonia is presented separately because of the very peculiar properties arising from molecular inversion. A consequence of inversion is that the effect depends on field intensity $E$ and pressure $p$ in a very different way from the other polar gases of symmetric top molecules, where it behaves as a function of the ratio $E/p$.

The component $\eta_3$ of viscosity [4] was measured by means of a capillary bridge which was brought out of balance by applying the electric field to two opposite branches, thereby altering their Poiseuille resistance [1]. An Atlas MMM membrane micromanometer was used to read the small pressure difference caused by such unbalance. The main results are the following:

a) the viscosity increases in an electric field (this is in contrast with all other gases studied so far, whose viscosity decreases in an external field, but in agreement with the behaviour of ammonia in a magnetic field [5]);

b) the effect is a function of $E^2/p$ in the pressure range studied (1.3 to 75 Torr for $NH_3$, 1.2 to 4.4 Torr for $ND_3$), in agreement with theory [6].

For $NH_3$, where saturation cannot be reached because of the high fields required, it is possible nevertheless to estimate the saturation value to be .00032, in surprisingly good agreement with the value found by KORVING in a magnetic field [5]. For $ND_3$, on the other hand, it was possible to measure quite precisely the saturation value, which is .00022, i. e. considerably smaller. The reason why the measurements are easier for heavy ammonia is that the fields required are proportional to the square root of the inversion frequency, which is 23.8 GHz in $NH_3$ and only 1.6 GHz in $ND_3$ [7].

The experimental points are shown in Fig. 1, where theoretical curves [6] are also plotted for comparison. Points corresponding to different pressures all fall on the same curve for each species. Since in the magnetic case the situation is much simpler and the relevant cross sections can be extracted directly from the experiments without relying too much on theoretical considerations, the average cross section of 133 Å² obtained by KORVING [5] has been used in drawing the theoretical curves. The curves are normalized to the saturation value. The agreement in the field values is good, indicating that the same collision processes are important in the magnetic and the electric problem and also that

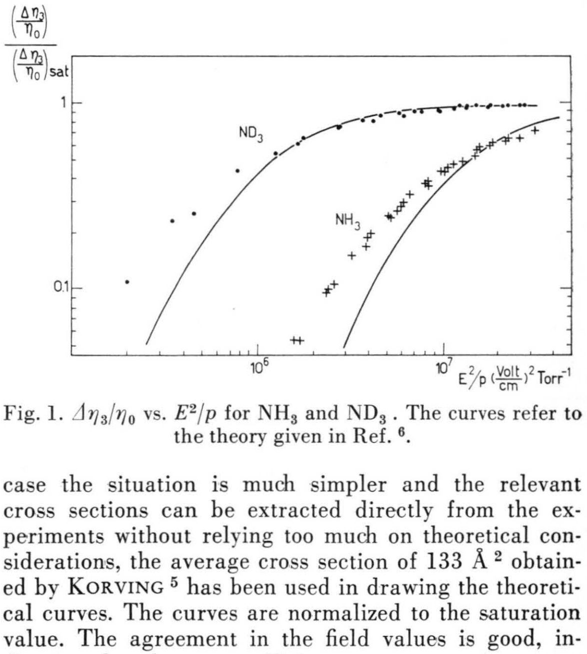

Fig. 1. $\Delta\eta_3/\eta_0$ vs. $E^2/p$ for $NH_3$ and $ND_3$. The curves refer to the theory given in Ref. [6].

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