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for by incomplete combination of the two components, so that a small quantity of water escapes further action of the gas by being enveloped in solid hydrate. A further proof of this is furnished by the fact that some preliminary experiments, in which little care was devoted to the complete formation of the hydrate by shaking, yielded far more oscillating values, which were all higher than those mentioned above. So it is beyond doubt that the values found can only indicate a too great content of water.

So the hydrate $H_2S.5H_2O$ differs from the many hydrates $M.6H_2O$ examined by VILLARD.

3. When in conclusion we survey the results of the investigation, it appears that the system $H_2S—H_2O$ presents great analogy to the system $SO_2—H_2O$, one of the gashydrate systems investigated by BAKHUIS ROOZEBOOM. The solubility of the hydrate of SO_2 under the three-phase pressure in the condensed gas is only small, like that of the hydrate of H_2S, because in both cases the pressure of the line SL_1G lies only little lower than the vapour tension line of the liquid, most volatile component. The other systems examined by BAKHUIS ROOZEBOOM deviate more or less from this system, either in consequence of the fact that the concentration of L_1 on SL_1G lies much less on one side, or because this line shows higher pressure than the two components, so that the L-G-surface presents a maximum in the isothermal sections.

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Physics. — "*On the inconsistency of my heat theorem and* VAN DER WAALS' *equation at very low temperatures.*" By Prof. W. NERNST of Berlin. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of May 27, 1911.)

Messrs. KOHNSTAMM and ORNSTEIN[1]) have published a criticism on my theorem of heat[2]) in these Proceedings, which is based on clearly mistaken premises, and which therefore calls for a refutation.

Everybody who has studied Thermodynamics, knows the form, in which HELMHOLTZ and others have expressed the second theorem of heat:

$$A—U = T\frac{dA}{dT}. \qquad \qquad (1)$$

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[1]) These Proc. of 24 Dec. 1910.

[2]) NERNST, Theoret. Chem. VI Aufl. S. 699 (1909); cf. also the literature mentioned in my paper, Journ. de Chim. Phys. 8 228 (1910).

Now the question rises how under certain conditions the two thermodynamic functions U and A (variation of the total and the free energy) behave at low temperatures, and in the discussion of this question I pointed out that when gases are present in the considered system, we cannot reach the absolute zero of temperature without discontinuities making their appearance, but that when only solid and liquid substances occur, the following equation holds:

$$lim \frac{dA}{dT} = lim \frac{dU}{dT} = 0, \; for \; T = 0 \; . \; . \; . \; . \; . \; (2).$$

The question what is the relationship between U and A for very low temperatures, has, moreover, already been treated by different authors[1]; hence it seemed superfluous to me to give further explanation about this problem itself.

In the strange way in which they treat the problem the two authors write that "it may be assumed" that the meaning is that the limit is approached with constant volume, because otherwise the whole problem would be indefinite.

It appears from this remark that the authors do not quite understand the meaning of equation (2), and though it seems hardly necessary, I shall illustrate the question of the way in which the limit is reached by an example. Let us consider the reaction

$$S \, (rhomb) \; \rightarrow \; S \, (mon) \, ;$$
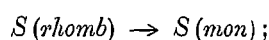
independently of the pressure under which the two modifications of the sulphur are, A possesses definite values, of course variable with the pressure. As equation (2) if it is correct, must also hold for the case of compression — and we come here to the conclusion that for low temperatures the heat of compression $A - U$ becomes equal to 0[2] — we need not impose any restriction on equation (2): only the differential quotient of A must of course in each special case be formed in the way that classical thermodynamics requires for equation (1). I can, however, not be expected to set this forth more fully here.

The authors now come to the conclusion in a rather circumstantial way, some points of which are by no means indisputable that when we consider VAN DER WAALS' formula to hold for fluids down to any temperature however low, equation (2) cannot hold.

This result, which, of course, I had known for a long time, may be arrived at in the following direct and exact way.

[1]) VAN 'T HOFF, BOLTZMANN Festschrift 1904 S. 233; Brönsted, Zeitschr. phys. Chem. 56 645 (1906).

[2]) NERNST, Journ. de Chim. Phys. 8 236 (1910).

As a case to which we will apply equation (2) we consider the expansion of a liquid from the volume v_1 to the volume v_2 at constant temperature. When VAN DER WAALS' formula

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \qquad \ldots \ldots \ldots (3)$$

holds for this, we get:

$$A = \int_{v_1}^{v_2} p \, dv = RT \ln \frac{v_2 - b}{v_1 - b} + \frac{a}{v_2} - \frac{a}{v},$$

while

$$U = \frac{a}{v_2} - \frac{a}{v_1}$$

follows for U. These relations are of course in harmony with equation (1), of which one can easily convince oneself, on the other hand we have:

$$\lim \frac{dA}{dT} = R \ln \frac{v_2 - b}{v_1 - b}, \; \lim \frac{dU}{dT} = 0 \; (\text{for } T = 0^{\cdot},$$

relations which are incompatible with equation (2), i.e. the new theorem of heat.

Now, however, it would be entirely injustifiable to consider the new theorem of heat refuted on this ground; it is indeed only experiment which has to decide this question. And as we know, experiment proved long ago that VAN DER WAALS' formula and even the general theory of corresponding states too are often in flagrant opposition to experiment [1]; it is further easy to see that especially at low temperatures the deviations become particularly striking. The new theorem of heat, on the other hand, has already been confirmed by a great number of examples, and in many hundreds of cases, in which we could not yet prove it with perfect exactness for want of a more accurate knowledge of specific heats at low temperatures, at least certain approximate results were confirmed, which I could derive from it.

For the rest it is also easy to derive from molecular theory even without having recourse to the new theory of indivisible units of energy which is of course incompatible with formula (3), that this formula cannot possibly hold for liquids at low temperatures. For it is known that strongly undercooled liquids assume a rigid glassy state at low temperatures according to TAMMANN's investigations, and nobody but

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[1] Cf. e.g. my Theoret Chem. p 236 and particularly Kristine Meyer, Zeitschr. physik. Chem. **32** 1, (1900).

Messrs. KOHNSTAMM and ORNSTEIN would ever think of applying VAN DER WAALS' formula to amorphous Quarz and similar substances. For here there is no longer present unchecked movement of the molecules, and this is entirely in conflict with the premises on which VAN DER WAALS' formula was derived. Indeed, the new theorem of heat is intended to account for the entirely different circumstances found here; for the rest it necessarily follows from the theory of indivisible units of energy [1]).

Messrs. KOHNSTAMM and ORNSTEIN therefore try to refute my theoretical considerations by evidently inaccurate, nay even inadmissible formulae [2]).

It is known that when TAIT questioned the second theorem of heat on the assumption of Demons, CLAUSIUS could point out with perfect justice that his formulae did not refer to the question how heat behaved with the aid of Demons, but what it did of its own accord. In the same way the attention of Messrs. KOHNSTAMM and ORNSTEIN might be drawn to the fact that equation (2) does not hold for substances which only exist in their imagination, and that the real behaviour of substances at low temperatures should be taken into account.

In conclusion we may point out that the formulae (2) express the whole of my theorem of heat, and that particularly the applications which I have made to *gaseous* systems, with which remarkably enough, the authors exclusively operate, consist only in a combination of these formulae and the already known theorems of heat.

Physics. — *"Further Experiments with Liquid Helium. E. A Helium-Cryostat. Remarks on the preceding Communications."* By Prof. H. KAMERLINGH ONNES. Comm. N°. 123ᵃ from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In the Jubilee volume presented in October 1910 to J. M. VAN BEMMELEN a description was given of an arrangement by means of which liquid helium had been successfully transferred from the apparatus in which it had been prepared to another vessel in which the measuring apparatus could be immersed in liquid helium. Advantage was then taken of this arrangement to

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[1]) NERNST, Journ. de Chim. Phys, 8 234 (1910); F. JÜTTNER, Zeitschr. f. Elektrochem. 17 139 (1911); O. SACKUR, Ann. d. Phys [4] 34 455 (1911).

[2]) With an analogous reasoning the said authors might also have "refuted" PLANCK's formula of radiation, the whole theory of indivisible units of energy etc.