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Curve $(L) = A + B + Ice + G = (M) + A + B$ has to coincide also with the (M) -curve, but it goes, starting from q towards lower temperatures.

Curve $(I) = A + B + L + G$ goes starting from q , also towards higher temperatures, but it must be situated below the curves (A) and (B) . In order to show this latter we take again the three points r , s and t in fig. 1. As the vapour-pressure increases, starting from s , along the isotherms rs and ts , the curves (A) and (B) must be situated, therefore, in fig. 3 above curve (I) .

Those considerations are also valid when we replace the components A and B by their hydrates A_m and B_n , provided that solution η is situated within the triangle WA_mB_n and not too close to the line A_mB_n . When this is really the case, then we are able to define the directions of the curves in the same way as e.g. in Comm. XIII.

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(*To be continued.*)

Physics. — “*On the equation of state of water and of ammonia*”

By G. HOLST. Supplement N^o. 41 *f* to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 27, 1917).

In an investigation published some time ago on the equation of state of methylchloride and ammonia¹⁾, it was shown that the sign of the coefficient C of KAMERLINGH ONNES'S²⁾ equation of state

$$pv = RT \left(1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \right)$$

was different for the two substances; for ammonia it was negative; for methyl chloride, as for other normal substances, C was found to be positive. At that time I ventured the hypothesis C would be found negative for other associating³⁾ substances. Following this idea I have calculated B and C for water vapour, starting from the data given by M. JACOB⁴⁾ in tables 7 and 8 of his paper on

¹⁾ G. HOLST. Comm. Leiden No. 144.

²⁾ See for instance H. KAMERLINGH ONNES and W. H. KEESOM. *Enc. d. Math. Wiss. Art. V* 10 p. 728. also Comm. Leiden Suppl. 23.

³⁾ *Comp. Enc.* p. 722, where it is pointed out that besides the associating (polymerized) substances, others occur (deviating substances) which show similar deviations as the first.

⁴⁾ M. JACOB. *Zeitschr. Ver. D. Ing.* 1912 p. 1980.

the specific heat and specific volume of water vapour. Calling the pressures given by JACOB in K.G./cm² p_j , the specific volumes in m³/K.G. v_j and the residual term of the equation of state

$$1000 v_j = \frac{4,706 T}{p_j} - R_j : R_j \text{ in dm}^3/\text{KG. we find:}$$

$$B + \frac{C}{v} + \dots = - \frac{R_j p_j v_j}{T} 0,17080$$

where $v = \frac{v_j}{1,2440}$.

When $-\frac{R_j p_j v_j}{T} 0,1708$ is drawn as a function of $\frac{1,2440}{v_j}$ a series of straight lines is obtained. From this diagram B and C can be immediately read as a function of the temperature. In this way the values were found given in the following table. (p. 934)

In the first place it will be seen that for water, as for ammonia, C is negative, and increases strongly with decreasing temperature. It is further clear that it will not be a simple matter to find a formula which represents C as a function of the temperature, all the more that there is nothing to guide us in the choice of the correct form of the function. As W. H. KEESOM told me that he and Miss VAN LEEUWEN had undertaken the deduction of a function of the kind required, I thought it advisable to await the result of this calculation before venturing upon the calculation of a purely empirical formula for myself.

For the other coefficient, B , there is something to go by: water, like ammonia, has a large dielectric constant, which is a temperature function.

We may therefore assume, with P. DEBYE¹⁾, that the water molecule has an electric moment. For spherical molecules with an electric bipole at the centre, W. H. KEESOM²⁾ has calculated the coefficient B as a function of the temperature. I will therefore compare the experimental values with those which KEESOM calculated. For this purpose, as suggested in Comm. Leiden Suppl. 25, we will draw F as a function of $\log hv$ and $\log B$ as function of $\log T$.

If the curves are shifted until they coincide over a fairly large range, we find for instance that $\log B = 7,35 - 10$ coincides with $F = 0,065$ and $\log T = 2,828$ with $\log hv = 0,358$.

¹⁾ P. DEBYE. Phys. Zeitschr. (13), 97, 1912. Comp. also J. KROO. Ann. d. Phys. (42), 1888, 1913.

²⁾ W. H. KEESOM. Comm. Leiden Suppl. 24b.

TABLE 1.

t	B	C
110	0.0157	-0.00120
120	-0.0146	-0.00095
130	-0.0135 ⁵	-0.00070
140	-0.0125 ⁵	-0.00053 ⁵
150	-0.0117 ⁵	-0.00039
160	-0.0111	-0.00023
170	-0.0103 ⁵	-0.00016 ⁵
180	-0.0097 ⁵	-0.00011 ⁵
190	-0.0091 ⁰	-0.00008 ⁰
200	-0.0085 ⁵	-0.00006 ⁵
220	-0.0075	-0.000036
240	-0.0065 ⁵	-0.000024
260	-0.0058	-0.000016
280	-0.0051	-0.000014
300	-0.0045	-0.000015
350	-0.0032	-0.000013
400	-0.0022 ⁵	-0.000012
450	-0.0015	-0.000010
500	-0.0010 ⁵	-0.000008
550	-0.0006 ⁵	-0.000006

As in ammonia, here also deviations show themselves at the lower temperatures (below 250° C.).

From these data, according to KRESOM's calculations, the radius and the dielectric moment can be derived for the water molecule, when assumed spherical.

In this way we find $\sigma = 3.21 \cdot 10^{-8}$ cm. and $m_e = 2.62 \cdot 10^{-18}$ in e.s. units.

Calculating these quantities for ammonia also, in the same way, I found $\rho = 3.54 \cdot 10^{-8}$ cm. $m_e = 2.36 \cdot 10^{-18}$ e.s. units.

The dimensions of the molecule, correspond, therefore, as regards the order of magnitude, with those determined in other ways.

For liquid water DEBYE has calculated the electric moment, and gives $m_e = 5.7 \cdot 10^{-19}$ e.s. units. The correspondence is not altogether what might be desired. I have therefore recalculated the electric moment from the measurements made by BAEDERER¹⁾, who determined the electric constant for water vapour and for ammonia. For water vapour the range of temperatures examined is very small, so that not much reliance was be put on the conclusions to be drawn.

According to DEBYE, the following formula applies to the dielectric constant

$$\epsilon = \epsilon_0 + \frac{a}{T}$$

where $a = \frac{4\pi m_e^2 N}{3k}$. N represents the number of molecules in 1 cm³., k PLANCK'S constant $1,346 \cdot 10^{-16}$ erg.

The first term ϵ_0 is due to the quasi-elastic electrons, the second to the bipoles. I have calculated the first from the index of refraction for which I took $n = 1,000255$ for water, and $n = 1,000377$ ²⁾ for ammonia. These values apply, it is true, to the visible spectrum, but the uncertainty introduced by this cannot be great, as ϵ_0 itself is small. In the following table the calculated values of $(\epsilon - \epsilon_0) \frac{q_0}{q} T$

will be found. The factor $\frac{q}{q_0}$ is introduced so as always to work with the same number of molecules.

The last column in the above table shows that for that part of the dielectric constant which is due to the bipoles, the same law holds as given by CURIE for the magnetic susceptibility, at least in the case of ammonia. The correspondence is not so good for water. At the same time, in order to be able to continue the calculation, I have assumed that the law applied to water also⁴⁾, using the mean constant in the calculation. In this way we find for the electric

¹⁾ K. BAEDERER Z. f. phys. Chem. (36), 305, 1901.

²⁾ See P. LANGEVIN. Ann. Chim. Phys. (5), 70, 1905.

³⁾ Recueil de Constantes Physiques.

⁴⁾ Whether deviations actually occur in water, as in magnetic substances, must be settled by further experiments.

Further, the question arises, why the value of the electric moment calculated for water vapour deviates from that calculated by DEBYE for the liquid. I thought the deviation might be accounted for by the fact that DEBYE has assumed in his

TABLE 2.
Dielectric constant for ammonia.

t	ϵ	$\frac{\rho}{\rho_0}$	ϵ_0	$\frac{\rho_0}{\rho} (\epsilon - \epsilon_0)$	$\frac{\rho_0}{\rho} (\epsilon - \epsilon_0) T$
18.4	1.00730	0.934	1.00070	0.00707	2.06
19.0	704	931	70	681	1.99
59.4	547	814	61	597	1.98
62.1	538	808	61	591	1.98
83.8	482	757	57	562	2.00 ^s
95.3	453	733	55	543	2.00
108.4	434	707	53	539	2.05 ^s

mean: 2.01

Dielectric constant for water vapour.

140.0	1.00765	0.645	1.00033	0.0115 ^s	4.7
142.2	767	641	33	114 ^s	4.7 ^s
143.2	736	640	33	110	4.6
145.8	694	636	32	104	4.4
148.6	648	632	32	097 ^s	4.1

mean: 4.5

moment of the water molecule $m_e = 2.3 \cdot 10^{-18}$ e.s. units, and for ammonia $m_e = 1.52 \cdot 10^{-18}$ e.s. units.

The order of magnitude is the same as the electric moment calculated from the equation of state. The numerical correspondence, however, still leaves something to be desired. This is not surprising,

calculation that the density of the liquid remained constant. His formula runs

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{T}{\rho} \rho_0 = \frac{4\pi m_e^2 N}{9k} + \frac{4\pi}{3} \sum \frac{N_i e^2}{f_i} T = a + 1T$$

in which for the calculation $\rho = \rho_0$ was assumed. If the necessary correction is introduced for the density, a becomes negative for water, so that no real value is found for the electric moment. So that in fact, like BOGUSLAWSKI (Phys. Zeitschr. 1914 p. 283) I could not find any agreement between theory and experiment for liquid water.

The form $\frac{\epsilon - 1}{\epsilon + 2}$, also, is not a very suitable one as soon as ϵ becomes much greater than 1. If, as in water, ϵ varies between 60 and 80, this fraction varies very little with changing ϵ .

as the measurements of the dielectric constant lie partially in the field of temperature, where the values for B calculated on the assumption of bipoles deviate from those determined experimentally, and moreover the supposition upon which the calculations are based will not entirely correspond to the facts.

Finally, I should like to draw attention to the conclusions, which follow from these calculations, for the determinations made by PH. A. GUYE¹⁾ and his fellow-workers of the molecular weight of gases from the weight of a litre under normal circumstances and the compressibility. These measurements, which have been made with the greatest care, have not always led to a satisfactory agreement between the molecular weight determined in this and in other ways, especially in the case of easily compressible gases. From our calculations it follows 1st that for an accurate determination of the compressibility the measurements must be so arranged that they enable us to determine²⁾ with the necessary accuracy not only B but also C ; and 2nd that when it is not established in another way that a given gas behaves as a normal substance, the compressibility for that gas must be specially determined.

Our calculations demonstrate that the deviations from the law of corresponding states, which in various substances may be very important as regards the value of B , may be even greater for C , so much so that the sign³⁾ for substances with and without bipoles may be different. The fact that for some gases including ammonia a correct value for the molecular weight was obtained by making use of the law of corresponding states, even where this was not to be expected according to the preceding discussion, must therefore be regarded as due to accident. And it is not to be expected that at other temperatures an equally good agreement would be found.

¹⁾ See for instance *Mém. de la Soc. de Phys. de Genève* (35) 1905—1907. and further *Journ. d. Chem. Phys.* various volumes.

²⁾ This conclusion was also drawn by H. KAMERLINGH ONNES and W. H. KEESOM *Enc. Math. Wiss.* V 10 p. 902. They also point out here (p. 900) the influence of the deviations from the law of the corresponding states upon the determinations of the molecular weight.

³⁾ Whereas B changes its sign for all substances examined, a possible difference of sign at equal reduced temperatures may thus be ascribed to the choice of the critical quantities as corresponding, this is not the case with C . For normal substances (see H. KAMERLINGH ONNES *Comm. Leiden* N^o. 74, p. 10) C is everywhere positive and increases with falling temperature.