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Physics. — “Some remarks on the values of the critical quantities in case of association.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 30, 1914).

1. Though this subject was treated already very fully by me in a paper in the Arch. TEYLER¹⁾ in 1908; and use was made afterwards (in 1909) of the contents of this paper in my Treatises on the Solid State²⁾ — I wish to make a few remarks induced by a paper by Prof. VAN DER WAALS in These Proceedings of April 1914 (p. 1076 et seq.) which may contribute to the removal of the pretty large difference found by him (p. 1081) for the volume value of CH₄ for methylalcohol (2,12) and for ethylalcohol (2,76).

VAN DER WAALS makes namely use of values of v_k , RT_k and p_k , of which he states (on p. 1078) that they would be exact by approximation. But it has appeared from the investigation made by me in 1908 that the “linear” dependence of the quantities RT_k and s of the association factor $2 : (1 + \beta)$ cannot be assumed even by approximation.

Not only does this hold when (as v. d. W. assumes) the volume of the molecules does not undergo any change on association; when in other words $\Delta b = -\frac{1}{2} b_2 + b_1 = 0$ — but the deviation in question presents itself to a much greater degree, when Δb is not = 0, as is certainly the case for water³⁾ and the alcohols.

In the cited TEYLER article I started from the equation

$$p = \frac{1 + \beta}{2} \frac{RT}{v - b} - \frac{a}{v^2}, \dots \dots \dots (1)$$

in which β represents the degree of dissociation of the double molecules, so that to the original $\frac{1}{2}$ double molecule are found $\frac{1}{2}(1 - \beta)$ double molecules and $\frac{1}{2} \cdot 2\beta = \beta$ single molecules, together $\frac{1}{2}(1 + \beta)$ molecules.

¹⁾ Arch. Teyler (2) T. XI, Troisième partie (1908): Théorie générale de l'association de molécules semblables et de la combinaison de molécules différentes. (p. 1—96).

²⁾ These Proc. of April 22, June 25, Aug. 31 1909; Nov. 24, 1910; Jan. 26 and June 23, 1911; resp. p. 765, 26, 120, 133, 454, 636 and 84. (See especially the third paper, p. 127—130).

³⁾ Already in 1899 I think I showed that the phenomenon of maximum density at 4° C. can be explained in a very simple way by the assumption of a negative value of Δb , so that a double molecule would have a larger volume than two single molecules. [Zeitschr. f. physik. Ch. 31 (Jubelband für VAN 'T HOFF)].

The quantity a appeared to have been left unchanged by the association, viz. $=a_1$ — the value for the case that all the molecules are single — everything referring to a single¹⁾ molecular quantity (e.g. 18 Gr. of H_2O , 46 Gr. of C_2H_6O , etc.). For we have evidently (the index 2 now refers, in distinction with my TEYLER article to the double molecules, the index 1 to the single molecules):

$$a = \left(\frac{1-\beta}{2}\right)^2 a_2 + 2 \times \frac{1-\beta}{2} \cdot \frac{2\beta}{2} a_{12} + \left(\frac{2\beta}{2}\right)^2 a_1,$$

in which $a_{12} = 2a_1$ and $a_2 = 4a_1$, so that we get:

$$a = (1-\beta)^2 a_1 + 2(1-\beta)\beta a_1 + \beta^2 a_1 = a_1.$$

Further:

$$b = \frac{1-\beta}{2} b_2 + \frac{2\beta}{2} b_1 = b_1 - (1-\beta)(-\frac{1}{2} b_2 + b_1) = b_1 - (1-\beta)\Delta b$$

$$\text{or } = \frac{1}{2} b_2 + \beta(-\frac{1}{2} b_2 + b_1) = \frac{1}{2} b_2 + \beta\Delta b.$$

The equation of state used by VAN DER WAALS (p. 1078) is identical with ours, as VAN DER WAALS starts from $1-x$ single molecules and x double molecules, together 1 mol., while we started from β single molecules and $(1-\beta):2$ double molecules, together $\frac{1}{2}(1+\beta)$ molecules. Accordingly we left the quantity of substance (viz. a single molecular quantity, e.g. 18 gr. of water etc.) constant, and varied the number of *molecules* on association from 1 to $\frac{1}{2}(1+\beta)$ — and VAN DER WAALS left the number of molecules constant $=1$, while he increased quantity of the substance from 1 to $1+x$.

If this is borne in mind, VAN DER WAALS's $v:(1+x)$ now passes into v' (now just as with us referring to a single molecular quantity of substance), and we get:

$$p = \frac{RT:(1+x)}{v'-b_1} - \frac{a_1}{v'^2},$$

in which therefore $1:(1+x)$ is identical with our $(1+\beta):2$, v' with our v , VAN DER WAALS putting $\Delta b=0$, and therefore identifying b with b_1 .

2. As β , the degree of dissociation of the double molecules, is a function of v , the dependence of the quantity β on v will have to be taken into account in order to find the values of the critical

¹⁾ In the cited TEYLER article I made everything refer to a *double* molecular quantity, but I think it more practical to continue to make the different quantities refer to a single molecular quantity. Hence all the quantities have now been divided by 2, resp. 4.

quantities in the determination of $\frac{\partial p}{\partial v} = 0$ and $\frac{\partial^2 p}{\partial v^2} = 0$. The calculations relating to this are pretty laborious, and were carried out in a separate chapter (§ 5 p. 25—34) in the cited TEYLER article (cf. also the above cited paper in These Proc. of Aug. 31, 1909, p. 127—130). We refer to this article, and give here only the results of the calculations — again making everything have reference to a single molecular quantity.

For v_k was found:

$$v_k = 3b_k \times \frac{m^2}{3m^2 - 2n}, \dots \dots \dots (2)$$

in which

$$\left. \begin{aligned} m &= 1 + \frac{1}{2}\beta(1-\beta)(1+\varphi)^2 \\ m &= 1 + \frac{3}{4}\beta(1-\beta)(1+\varphi) + \frac{1}{8}\beta(1-\beta)(1-3\beta^2)(1+\varphi)^2 \end{aligned} \right\} \dots (3)$$

while

$$\varphi = (1+\beta) \frac{\Delta b}{v-b} \dots \dots \dots (4)$$

(p. 26 and 29 loc. cit.).

When $\Delta b = 0$ and so also $\varphi = 0$, as VAN DER WAALS assumes, even then remains:

$$\left. \begin{aligned} m &= 1 + \frac{1}{2}\beta(1-\beta) = (1+\beta)(1-\frac{1}{2}\beta) \\ m &= 1 + \frac{3}{4}\beta(1-\beta) + \frac{1}{8}\beta(1-\beta)(1-3\beta^2) = (1+\beta)^2(1-\frac{3}{8}\beta + \frac{3}{8}\beta^2) \end{aligned} \right\} \dots (3^a)$$

through which for v_k , with

$$3m^2 - 2n = (1+\beta)^2(1-\frac{3}{4}\beta),$$

is found:

$$v_k = 3b_1 \times \frac{(1-\frac{1}{2}\beta)^2}{1-\frac{3}{4}\beta} \dots \dots \dots (2^a)$$

In this the factor 3 must of course be replaced by a smaller one (e.g. 2,1), when b is a function of v , and varies between b_∞ and b_0 , when v varies from ∞ to v_0 .

With regard to the *factor* of $3b_k$ — which according to VAN DER WAALS (referring namely to a single molecular quantity and *not* to a $1+x$ times larger quantity) would remain constant = 1 (at least by approximation) — we see immediately that this factor can differ pretty considerably from unity. For $\beta = 0$ (only double molecules) and $\beta = 1$ (only single molecules) the factor is properly = 1, but for $\beta = \frac{2}{3}$ it has the *minimum value* $\frac{8}{9}$. And this deviation, which already amounts to $\frac{11}{90}$, is still more pronounced when Δb is *not* = 0, but has e.g. a *negative* value.

For RT_k we have found (p. 31 loc. cit.), again referring to a single molecular quantity:

$$RT_k = \frac{8 a_1}{27 b_k} \cdot \frac{2}{1+\beta} \times \frac{n^2(3m^2-2n)}{m^5}, \dots \dots \dots (5)$$

which with $\Delta b = 0$ passes into

$$RT_k = \frac{8 a_1}{27 b_1} \cdot \frac{2}{1+\beta} \times \frac{(1+\beta)(1-\frac{1}{8}\beta + \frac{3}{8}\beta^2)^2(1-\frac{3}{4}\beta)}{(1-\frac{1}{2}\beta)^5} \dots \dots \dots (5^a)$$

If $\beta = 1$ (single molecules), then RT_k duly becomes $= \frac{8 a_1}{27 b_1}$,

but for $\beta = 0$ (double molecules) RT_k becomes $= 2 \times \frac{8 a_1}{27 b_1}$.

But it is again immediately seen that RT_k certainly does not linearly change with $2:(1+\beta)$, i.e. with VAN DER WAALS'S $1+x$, as the latter assumes on p. 1078 of his treatise.

For the remaining factor is indeed again $= 1$ for $\beta = 0$ and $\beta = 1$, but it is $3456 : 3125 = 1,106$ for $\beta = \frac{1}{3}$; $= 1445 : 1296 = 1,115$ for $\beta = \frac{1}{2}$; and $= 1125 : 1024 = 1,099$ for $\beta = \frac{2}{3}$. The deviation can therefore again amount to $\frac{9}{100}$, in comparison with 11% for v_k , but in opposite direction. This deviation too is more pronounced, when Δb differs from 0.

With regard to the value of p_k , at last, we find:

$$p_k = \frac{1 a}{27 b_k^2} \times \frac{(3m^2-2n)^2(4n-3m)}{m^5}, \dots \dots \dots (6)$$

passing into

$$p_k = \frac{1 a}{27 b_1^2} \times \frac{(1-\frac{3}{4}\beta)^2(1+\beta-3\beta^2+\frac{3}{2}\beta^3)}{(1-\frac{1}{2}\beta)^5}, \dots \dots \dots (6a)$$

when $\Delta b = 0$. For

$$4n-3m = (1+\beta)(1+\beta-3\beta^2+\frac{3}{2}\beta^3).$$

The factor of $\frac{1 a}{27 b_1^2}$ duly has the value 1 both for $\beta = 0$ and $\beta = 1$; but becomes $= 4617 : 3125 = 1,477$ for $\beta = \frac{1}{3}$; $= 375 : 243 = 1,543$ for $\beta = \frac{1}{2}$; and $= 189 : 128 = 1,476$ for $\beta = \frac{2}{3}$.

Accordingly the deviation from unity is very considerable — for $\beta = \frac{1}{3}$, more than $\frac{54}{100}\%$. Hence there is no longer any question of an approximate equality to $\frac{1 a}{27 b_1^2}$, as VAN DER WAALS supposes he may assume. (p. 1078 l.c.). And this amount can still increase for $\Delta b \text{ not} = 0$.

¹⁾ If it is taken into account that $a_1 = \frac{1}{4} a_2$, $b_1 = \frac{1}{2} b_2$, RT_k becomes as it always did $= \frac{8 a_2}{27 b_2}$, in which a_2 and b_2 now refer to a double molecular quantity.

It is therefore self-evident that when the quantities $s = RT_k : p_k v_k$ and $T_k : p_k$ are calculated, which occur in VAN DER WAALS'S considerations, no linear dependence on $2 : (1 + \beta)$, resp. $1 + x$ is to be expected there either.

3. Now

$$s = \frac{RT_k}{p_k v_k} = \frac{8}{3} \cdot \frac{2}{1 + \beta} \times \frac{n^2}{m^2 (4n - 3m)} \dots \dots \dots (7)$$

is found for the quantity s , passing (with $\Delta b = 0$) into

$$s = \frac{8}{3} \cdot \frac{2}{1 + \beta} \times \frac{(1 + \beta) (1 - \frac{2}{3} \beta + \frac{3}{8} \beta^2)^2}{(1 - \frac{1}{2} \beta)^2 (1 + \beta - 3\beta^2 + \frac{3}{2} \beta^3)} \dots \dots (7a)$$

For $\beta = 1$ (all simple molecules) s becomes $= s_0 = \frac{8}{3}$ (or $= 3,77$, when b varies with v), and for $\beta = 0$ (all double molecules) s becomes $= \frac{8}{3} \times 2$, hence twice the value. But here too we remain very far from linear dependence.

For $\beta = \frac{1}{3}$, we find namely for the last factor in (7a) the value $384 : 475 = 0,808$; for $\beta = \frac{1}{2}$ the value $280 : 360 = 0,803$; and for $\beta = \frac{2}{3}$ the value $375 : 448 = 0,837$. Hence a difference of about 20% for $\beta = \frac{1}{3}$.

On account of the importance of the accurate knowledge of the value of the quantity s for associating substances, I have calculated the following table.

β	$\frac{2}{1 + \beta} = 1 + x$	Factor	$\frac{2}{1 + \beta} \times \text{factor} = \frac{s}{s_0}$
0	2	1	2
0.1	1.818	0.903	1.642
0.2	1.667	0.847	1.412
0.3	1.538	0.815	1.253
0.35	1.481	0.805	1.192
0.4	1.429	0.801	1.145
0.5	1.333	0.803	1.071
0.6	1.250	0.820	1.025
0.7	1.176	0.849	0.998
0.8	1.111	0.890	0.989 (min)
.9	1.053	0.945	0.995
1	1	1	1

Instead of a regular linear decrease with $2:(1+\beta)$, i.e. with $1+x$, values are even seen to appear < 1 in the neighbourhood of $\beta = 1$ (all the molecules single), with a *minimum* at about $\beta = 0,8$ (accurately at $\beta = 0,8015$), and a horizontal final direction, i.e.

$$\frac{d}{d\beta} \left(\frac{s}{s_0} \right) = 0.$$

On increasing association (β from 1 to 0), s will therefore first become somewhat smaller than s_0 ($= 3,77$ for "ordinary" substances), and then (from $\beta = 0,7$) $s:s_0$ will become greater than 1, and increase to 2 for $\beta = 0$, when the association to double molecules is perfect.

A straight line for $s:s_0$ (as VAN DER WAALS thinks) therefore replaced by a line that is pretty considerably curved downward between the values 2 and 1 with a minimum close to 1, so that $s:s_0$ at first decreases there instead of increasing.

What consequences this behaviour will have with respect to the *degree of association* β , calculated from the value found for s for *methylalcohol*, viz. 4,52, may appear from what follows.

As $s:s_0 = 4,52:3,77 = 1,2$, we should find about $\beta = 0,67$ or $x = 0,2$ for β , according to the second column of the above table, when we were led by a supposed linear dependence. But when we also take account of the "factor" by the side of $2:(1+\beta)$, we find about $\beta = 0,35$ or $x = 0,5$ from the last column for the value for β answering to the ratio $s:s_0 = 1,2$.

A difference, in fact, too large to be neglected. Instead of 0,8 single molecules to 0,2 double molecules, as VAN DER WAALS would find with his linear dependence, we find more accurately 0,5 single molecules to 0,5 double ones. The relation $x:(1-x)$ has become 1 instead of 4.

4. The second quantity which plays a part in the cited paper by VAN DER WAALS, is the quantity $T_k:p_k$, which may be put proportional to the molecule size for non-associating substances. We now find for it:

$$\frac{T_k}{p_k} = \frac{8}{R} b_1 \cdot \frac{2}{1+\beta} \times \frac{(1+\beta) (1 - \frac{3}{8}\beta + \frac{3}{8}\beta^2)^2}{(1 - \frac{3}{4}\beta) (1 + \beta - 3\beta^2 + \frac{3}{2}\beta^3)}, \dots (8a)$$

which with $\Delta b = 0$ passes into

$$\frac{T_k}{p_k} = \frac{8}{R} b_k \cdot \frac{2}{1+\beta} \times \frac{n^2}{(3m^2 - 2n) (4n - 3m)} \dots (8)$$

We shall not discuss the course of this again, but solve from this

the required value of $\frac{8}{R} b_k$. By means of (7) and (8) we find easily:

$$(b) = \frac{8}{R} b_k = \left(\frac{T_k}{p_k} : \frac{s}{s_0} \right) \times \frac{3m^2 - 2n}{m^2}, \dots \dots \dots (9)$$

or when $\Delta b = 0$:

$$(b) = \frac{8}{R} b_1 = \left(\frac{T_k}{p_k} : \frac{s}{s_0} \right) \times \frac{1 - \frac{3}{4}\beta}{(1 - \frac{1}{8}\beta)^2} \dots \dots \dots (9^a)$$

When therefore the value of β has been found from (7) and (7a), it can be substituted in (9) or (9a), and $\frac{8}{R} b_1$ is known.

According to VAN DER WAALS, (b) would be $= 6,52 : 1,2 = 5,43$ for methylalcohol, whereas (for $\Delta b = 0$) the more accurate value with $\beta = 0,35$ (see above) would amount to $5,43 \times 1,084 = 5,89$.

This value is still larger than that found by VAN DER WAALS, and would yield $7,55 - 5,89 = 1,66$ for CH_2 , instead of 2,12. And when $\Delta b = 0$ is assumed, the accurate value of (b) will be larger than the approximate one for every value of β , because $1 - \frac{3}{4}\beta$ is always $> (1 - \frac{1}{8}\beta)^2$.

It is, however, easy to see that when not (7a) and (9a) are used for the calculation resp. of β and (b), a value < 1 , e. g. 0,88 can very well be found for the factor $(3m^2 - 2n) : m^2$ in (9), through which 5,43 would diminish to 4,78, so that $7,55 - 4,78 = 2,77$ would be found for CH_2 , in good harmony with the value found for ethylalcohol.

Now $(3m^2 - 2n) : m^2$ becomes < 1 , when

$$3 - \frac{2n}{m^2} > 1 \quad \text{or} \quad m^2 < n.$$

I. e. with a view to (3)

$$[1 + \frac{1}{2}\beta(1-\beta)(1+\varphi)^2] < 1 + \frac{3}{4}\beta(1-\beta)(1+\varphi) + \frac{1}{8}\beta(1-\beta)(1-3\beta^2)(1+\varphi)^3$$

must be, i. e.

$$\beta(1-\beta)(1+\varphi)^2 + \frac{1}{4}\beta^2(1-\beta)^2(1+\varphi)^4 < < \frac{3}{4}\beta(1-\beta)(1+\varphi) + \frac{1}{8}\beta(1-\beta)(1-3\beta^2)(1+\varphi)^3,$$

or

$$(1+\varphi) + \frac{1}{4}\beta(1-\beta)(1+\varphi)^3 < \frac{3}{4} + \frac{1}{8}(1-3\beta^2)(1+\varphi)^2,$$

or also

$$6 - 8(1+\varphi) + (1-3\beta^2)(1+\varphi)^2 - 2\beta(1-\beta)(1+\varphi)^3 > 0.$$

If β were $= 0$, then φ would have to be $< 3 - \sqrt{10}$, i. e. $< -0,162$. If β were $= \frac{1}{2}$, then φ ought to be $<$ about $-0,25$. And if β were $= 1$, then φ would have to be $< -3 + \sqrt{7}$, i. e.

$< -0,354$. As now according to (4) $\varphi = (1 + \beta) \Delta b : (v - b)$, we have also :

$$\varphi = (1 + \beta) \frac{\Delta b}{b} \frac{b}{v-b}.$$

For T_k , with $v = 2b$, the value $\varphi : (1 + \beta)$ follows from this for $\Delta b : b$. For β resp. $= 0, \frac{1}{2}$, and 1 we find therefore resp. the values $< -0,16$, $< -0,167$ and $< -0,177$ from this. When accordingly $\Delta b : b$ becomes smaller than about $-\frac{1}{6}$, the value of the factor $(3m^2 - 2n) : m^2$ can become < 1 . For a value $0,88$ (see above) it will therefore be necessary that $-\Delta b : b$ be about $0,2$ — a value which in view of the value for H_2O (which has been found of the same order of magnitude) is not at all impossible for methyl-alcohol either.

At any rate it is seen from the above, that for associating substances (b) cannot be put simply proportional to $(T_k : p_k) : (s : s_0)$, but that the factor $(3m^2 - 2n) : m^2$ must be taken into account. Nor may for the calculation of β from $s : s_0$ simply $2 : (1 + \beta) = 1 + x$ be written for the latter ratio; another factor $n^2 : m^2 (4n - 3m)$ must be added to it, which factor amounts to about $0,8$ (see the above table) in the case $\Delta b = 0$ between $\beta = 0,3$ and $\beta = 0,5$ or $0,6$, which differs too much from 1 to be neglected.

The error made by VAN DER WAALS is according to § 2 owing to this, that he believed he could assume values for $RT_k : (1 + x)$ and p_k , which do not differ (at least differ little) from the corresponding values for non-associating substances.

The calculation (given by me already in the cited TEYLER-article in 1908) teaches something entirely different: for p_k (with $\Delta b = 0$) e.g. the deviation can amount to more than 54% .

The finding of a too large value for $(T_k : p_k) : (s : s_0)$, viz. $5,43$ instead of about $4,8$ points out, that necessarily for CH_3OH the quantity $\Delta b : b$ will have a pretty large negative value, namely about $-0,2$. If β were about $\frac{1}{3}$, then b would be $= (1 - \beta) \frac{1}{2} b_2 + \beta b_1 = \frac{1}{3} b_2 + \frac{1}{3} b_1$, and from

$$\frac{\Delta b}{b} = \frac{-\frac{1}{2} b_2 + b_1}{\frac{1}{3} b_2 + \frac{1}{3} b_1} = -0,2$$

would follow $16 : 13 = 1,23$ for the ratio $\frac{1}{2} b_2 : b_1$, i. e. the double molecules would be about $1,23$ times as large as two single molecules — which is by no means impossible.

5. On this occasion I will draw attention at the same time that in § 7, p. 40—42 of the cited TEYLER-article also the quantity

$f = \left(\frac{T}{p} \frac{dp}{dT} \right)_k$ for associating substances has been calculated by me. When the heat of dissociation q of the double molecules may be put $= 0$, we find for f (see formula (28) loc. cit.):

$$f = f_0 \times \frac{n}{4n - 3m},$$

or when $\Delta b = 0$:

$$f = f_0 \times \frac{(1 - \beta)(1 - \frac{1}{2}\beta + \frac{1}{2}\beta^2)}{1 + \beta - 3\beta^2 + \frac{1}{2}\beta^3},$$

in which the factor of f_0 both for $\beta = 0$ and for $\beta = 1$ again assumes the value 1. For $\beta = \frac{1}{2}$ the value is, however, $16:19 = 0,84$, which would make the normal value 7 descend to about 5,9. As f for methylacohol is found > 7 , namely \approx about 8,6 (cf. KUENEN, Die Zustandsgleichung, p. 142, where the value $3,75 \times 2,30$ is given), the factor of f_0 would have to be about 1,2 instead of 0,84; i. e. $\Delta b \neq 0$, and again *negative* — or also the value of q (see the full formula in TEYLER, p. 42) would moreover have to be different from 0, and that *positive*.

Fontainivent sur Clarens, May 1, 1914.

Physics. — “On apparent thermodynamic discontinuities, in connection with the value of the quantity b for infinitely large volume.” By DR. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 27, 1914).

1. One of the principal results of the foregoing series of communications¹⁾ has been this (cf. particularly II p. 926 and IV p. 464), that the quantity b_g , i. e. the value of b for infinitely large volume (hence in the ideal gas state) cannot possibly be $= 4m$ as the classical kinetic theory gives for it. With decreasing temperature b_g approaches namely more and more to b_0 . If in the ideal gas state b_g were $= 4m$, b_g would have to be $= 4m$ also at very low temperature (this kinetic result holds namely independent of the temperature), while in the condensed liquid state with cubic arrangement e. g. of the molecules, supposed to be spherical, b_0 would be about $= 2m'$, in which m' is either equal to or smaller than m , so that then b_g cannot possibly become $= b_0$.

¹⁾ These Proc. of March 26, April 23, May 29 and Sept. 26, 1914 (to be cited as I–IV).