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alcoholic solution of the salt in a trough, which contained platinum electrodes 2 cm distant from each other. A potential difference of 100 volt was applied. At 18° the current density was 75 milliamp./cm² and in the viscous solution just above the freezing point of aethyl-alcohol (−118°) 30 milliamp./cm². I also worked with a dilute solution in amyl-alcohol (−134°). With a spectral apparatus of very great dispersion I observed in this case considerably broadened and diffuse absorption bands, the aspect of which did not change when the current was made. It must be remarked however that under these circumstances the velocity of the negative ion is very small as yet.

Physics. — “*The calculation of the molecular dimensions from the supposition of the electric nature of the quasi-elastic atomic forces*”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 31, 1914).

1. In four papers¹⁾, in which some new relations between the critical quantities were given, I have also tried to determine the form of the function $b = f(v, T)$. While the dependence of b on the volume appeared to be pretty intricate — that namely the found relations at the critical point and at the same time the limiting condition at $v = v_0$ be satisfied — the dependence on the temperature could be given by a very simple relation, namely (see III, p. 1053, formula (36)):

$$\frac{b_g - (b_0)}{(b_0)} = 0,041 \sqrt{T}, \dots \dots \dots (1)$$

in which (b_0) represents the value of the limiting volume $b_0 = v_0$, extrapolated from the direction of the so-called straight diameter at T_k . This formula was an extension of that which was found at the critical point, namely (loc. cit. p. 1051):

$$\frac{b_k - (b_0)}{(b_0)} = 2\gamma_k - 1 = 0,038 \sqrt{T_k}, \dots \dots \dots (2)$$

in which γ_k is the coefficient of direction of the “straight diameter” in the neighbourhood of the critical point. The table (p. 1052) calculated to support this relation may be reproduced here.

¹⁾ These Proc. of March 26, April 23, May 29 and Sept. 26, 1914.

	T_k	$\sqrt{T_k}$	$2\gamma_k - 1$	γ_k calculated	γ_k found
Helium	5.2	2.28	0.0866	0.543	± 0.56
Hydrogen	32.3	5.68	0.2158	0.608	0.604
Argon	150.65	12.27	0.4763	0.738	0.745
Xenon	289.7	17.02	0.6468	0.823	0.813
Acetylene	308.5	17.56	0.6673	0.834	0.858
Isopentane	460.9	21.47	0.8159	0.908	0.914
Fluorbenzene	559.6	23.66	0.8991	0.950	0.933

We have already repeatedly pointed out, that both the form of the function $b = f(v)$, and the form of the temperature function $b = f(T)$ suggest that the change of b chiefly, probably even exclusively, corresponds to a *real* volume change of the molecules, and that an apparent change in consequence of the partial overlapping of the so-called distance spheres must be rejected. (See among others IV, p. 464).

That such an apparent change loses all foundation in consequence of the non-existence of the relation $b = 4m$, has been conclusively proved by me in my opinion in a later article (These Proceedings of Nov. 7, 1914). We found there namely (see p. 611), that in consequence of the influence of the (infinitely slight) quasi-association at $v = \infty$ the quantity b must be diminished by the *finite* quantity $R:C$. ($C =$ the "constant" of the quasi-association). Considerations of another nature made it probable that b must, indeed, be identified in all cases with the real molecular volume m , at most increased by a certain influence sphere.

2. We have already seen that the found temperature relation agrees perfectly with that given by a formula drawn up by VAN DER WAALS already much earlier for the variability of b , viz.

$$[p + a/v^2 + A(b-b_0)](b-b_0) = fRT, \quad \dots \quad (3)$$

in which A represents the (spacial) constant of the quasi-elastic atomic forces, which atomic forces were put proportional to the increase of volume $b - b_0$. The quantity f is a coefficient which depends on the number of degrees of freedom.

After substitution of $RT:(v - b)$ for $p + a/v^2$, and elimination of A and T , formula (3) appeared, however, *not* to satisfy the relation $b = f(v)$ found by us. (See particularly II, p. 930 in con-

nection with II, p. 931 and III, p. 1048, where the probable form for this relation was given). If, however, we do not enter into a further consideration of the extra-molecular part $(p + a/v^2)(b - b_0)$, and for the present examine only the intra-molecular part $A(b - b_0)^2$, we can, in connection with some plausible supposition concerning A , examine what conclusions might be derived from it with regard to the absolute size of the molecules, and whether the found dimensions agree with the molecular dimensions derived from other data.

The simplest supposition concerning A is, that the quasi-atomic forces are brought about under the influence of two elementary-charges e , so that for the (linear) constant of the atomic forces, following LINDEMANN (see among others Conseil SOLVAY, German edition of 1914, p. 286; and also pp. 316—317, as far as the derivation from THOMSON'S atom model is concerned),

$$F_0 = \frac{Nne^2}{d^3} \dots \dots \dots (4)$$

may be written, in which N represents the number of molecules per gr. mol., n the valency of the atoms, sub-atoms or atom groups, and d the equilibrium distance of the charges. If further the deviation is σ , the atomic force for not too great values of σ is represented by

$$F = F_0 \sigma,$$

and the term of the energy corresponding to $A(b - b_0) \times b - b_0$ by $F_0 \sigma \times \sigma$.

According to (4) we can now write for $F_0 \sigma^2$:

$$F_0 \sigma^2 = \frac{Nne^2}{d^3} \sigma^2, \quad 1)$$

or also when s_0 is the smallest diameter of the molecules (i.e. with a deviation of the atoms $\sigma = 0$):

$$F_0 \sigma^2 = \frac{Nne^2}{s_0^3} \left(\frac{s_0}{d}\right)^3 \sigma^2.$$

If we assume a spherical shape for the molecules (if this it not the case, we can yet assume a *mean* diameter s_0 , so that m becomes $= \frac{1}{6} \pi s_0^3$), we may write:

$$F_0 \sigma^2 = \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^3 \frac{1}{(\frac{1}{6} \pi s_0^3)^2} (\frac{1}{6} \pi s_0^2 \sigma)^2 = \frac{1}{36} \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^3 \frac{1}{b_0^2} (b - b_0)^2 \sigma,$$

in which b_0 is the smallest volume of the molecules. The quantity

1) We may point out here, that in consequence of the dimensions of e , viz. gr.^{1/2} cm.^{1/2} sec.⁻¹ (in electrostatic units), $F_0 \sigma^2$ properly gets the dimensions of an energy.

θ , which differs little from 1, has been written by the side of $(b - b_0)^2$, because $\pi s_0^2 \sigma$ represents $b - b_0$ only when σ is very small. Else we have:

$$b - b_0 = \frac{1}{6} \pi (s_0 + 2\sigma)^3 - \frac{1}{6} \pi s_0^3 = \frac{1}{6} \pi (6s_0^2\sigma + 12s_0\sigma^2 + 8\sigma^3),$$

so that evidently θ represents:

$$\theta = [\pi s_0^2 \sigma : \frac{1}{6} \pi (6s_0^2\sigma + 12s_0\sigma^2 + 8\sigma^3)]^2 = (1 + 2\sigma/s_0 + \frac{4}{3}\sigma^2/s_0^2)^{-2} = (1 + \sigma/r_0 + \frac{1}{3}\sigma^2/r_0^2)^{-2},$$

when r_0 represents the smallest radius of the molecule $= \frac{1}{2} s_0$ (for $\sigma = 0$).

For a substance like Argon, where $b_k : b_0 = 2\gamma_k = 1,5$, $r_0 + \sigma$ would e. g. be $= r_0 \sqrt[3]{1,5} = 1,145 r_0$, hence $\sigma/r_0 = 0,145$, and $\theta = (1,152)^{-2} = 0,75$ (for $b_k - b_0$).

For substances as Fluorbenzene, where $b_k : b_0 = 1,9$, $\sqrt[3]{1,9}$ becomes $= 1,239$, and thus $\sigma/r_0 = 0,239$, $\theta = (1,258)^{-2} = 0,63$. For H_2 and He values will be found nearer 1. Thus for He , where $b_k : b_0 = 1,12$, we get $\sigma/r_0 = 0,0385$, $\theta = (1,040)^{-2} = 0,92$. For H_2 we have $b_k : b_0 = 1,2$, so $\frac{\sigma}{r_0} = 0,063$, $\theta = (1,067)^{-2} = 0,80$. All these

values refer to the case that (for T_k) the atoms (sub-atoms, atomic groups) in the molecule have almost the greatest deviation, as b_k does not differ much from b_g . We shall presently have to take this factor θ into account.

When we compare the found expression for $F_0 \sigma^2$ with the term $A(b - b_0)^2$ in (3), we get for the present:

$$A = \frac{1}{36} \theta \frac{Nne^2}{s_0} \left(\frac{s_0}{d}\right)^3 \frac{1}{b_0^2}, \dots \dots \dots (5)$$

so that the quantity A in (3), in consequence of the introduction of $b - b_0$, through θ appears to be dependent on the extent of the deviation in a slight degree — in opposition to the quantity F_0 in (4), in which the original deviation σ occurs. Hence A is (in a slight degree) both a function of the volume and of the temperature.

Now for infinite volume, according to (3):

$$A_g (b_g - b_0)^2 = fRT,$$

while according to (1):

$$\frac{b_g - (b_0)}{(b_0)} = 0,041 \sqrt{T},$$

in which, as has been said, (b_0) does *not* represent the real limiting volume $b_0 = v_0$, but the limiting volume extrapolated from the direction of the straight diameter at T_k . We saw in IV, p. 458—459, that e.g. for Argon b_0 is $= 0,305 v_k$, whereas $(b_0) = 0,286 v_k$. From

$(b_g - (b_0)) : b_0 = 0,041 \sqrt{T}$ follows that for Argon, where $\sqrt{T_k} = 12,27$, $b_g : (b_0) = 1,503$. Hence for $b_g : b_0$ would be found $1,503 : 1,066 = 1,410$, because $b_0 : (b_0) = 0,305 : 0,286 = 1,066$. Hence the value of $(b_g - b_0) : b_0$ is $0,410$, so that for T_k this value can be represented by $(0,410 : 12,27) \sqrt{T_k} = 0,0334 \sqrt{T_k}$; and we can, therefore, write — at least for Argon — instead of (1):

$$\frac{b_g - b_0}{b_0} = 0,0334 \sqrt{T} \quad (1^a)$$

From $A_g (b_g - b_0)^2 = fRT$ and (1^a) now follows:

$$A_g = \frac{fR}{(0,0334)^2 b_0^2} = 896 \frac{fR}{b_0^2}, \quad (6)$$

in which, as appears from the derivation of (5) from (4), the coefficient 0,0334 will still depend with A_g on T through θ_g in a slight degree, and is strictly speaking only valid at T_k , i.e. the temperature at which we calculated just now this coefficient from that of equation (1).

Combination of (5) and (6) now gives immediately:

$$s_0 \left(\frac{d}{s_0} \right)^3 = \frac{^{1/3} \theta_g \cdot N n e^2}{896 f R} = \theta_g \frac{n^{1/3} \times 6 \cdot 10^{23} \times (4,825 \cdot 10^{-10})^3}{896 \times 83,15 \cdot 10^6}.$$

In this $(4,825 \cdot 10^{-10})^3 = 23,28 \cdot 10^{-20}$, and we find:

$$s_0 \left(\frac{d}{s_0} \right)^3 = \theta_g \frac{n}{f} \cdot \frac{3 \cdot 88 \cdot 10^3}{7,45 \cdot 10^{10}} = \theta_g \frac{n}{f} \times 5,21 \cdot 10^{-8} \quad . . . (7)$$

For N , AVOGADRO'S value, we have substituted, the most probable one, viz. $6,0 \cdot 10^{23}$ for N , as it follows both from PLANCK'S theory of radiation and from the values directly determined by MILLIKAN and NORDLUND. If we namely put for WIEN'S constant of radiation $c_2 = c(h : k)$ the middle value of WARBURG and COBLENTZ, viz. 1,441, and for STEFAN-BOLTZMANN'S constant a the mean value of WESTPHAL and several others, viz. $7,6 \cdot 10^{-15}$, we find from the wellknown formulae for h and k :

$$\beta = h : k = 4,80 \cdot 10^{-11} ; k = 1,393 \cdot 10^{-16} ; h = 6,690 \cdot 10^{-27}.$$

For N we find therefore $83,15 \cdot 10^6 : 1,393 \cdot 10^{-16} = 5,97 \cdot 10^{23}$ from $R = N \times k$. MILLIKAN'S value is $6,06 \cdot 10^{23}$; NORDLUND'S is $N = 5,91 \cdot 10^{23}$ (Z. f. Ph. Ch. **87**, p. 62). The mean of these three values is $5,98 \cdot 10^{23}$, so that with some probability we may assume about $6,0 \cdot 10^{23}$ for N .

For $N \times e$ has been found $107,88 : 0,0011180 = 96494$ Coulomb = $9649,4$ electromagnetic units = $2,895 \cdot 10^{14}$ electrostatic units. Hence we find for the value of the electric elementary quantum e after division by N the value $4,825 \cdot 10^{-10}$.

3. We may now proceed to compare the value of s_0 , found in (7), with the values of s_0 calculated by other methods.

If we put $n=1$, $f=1$, so monovalent atoms or atom groups, resp. subatoms, and three degrees of freedom¹⁾ corresponding to the spacial conception of the molecular vibrators, then:

$$s_0 \left(\frac{d}{s_0} \right)^3 = \theta_g \times 5,21 \cdot 10^{-8},$$

in which θ_g represents the value of θ at the greatest deviation of corresponding to b_g (accurate at T_k). And because we have calculated above the coefficient 0,0334 in (1^a) from data concerning Argon, we shall also now substitute the value, which we have found for Argon, viz. 0,75 (also at T_k) for θ_g . Hence

$$s_0 \left(\frac{d}{s_0} \right)^3 = \pm 3,9 \cdot 10^{-8} \text{ cM.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

in which the found value 3,9 will hold by approximation for all substances on account of the generality of our considerations — at least for substances with not too complex molecules, where also the values of s_0 appear to differ only little.

Let us now calculate the values for s_0 for Argon, Hydrogen, and Helium. The values given before for them are most of them inaccurate, partly in consequence of the value of N , which was assumed too high (viz. $6,82 \cdot 10^{23}$ according to PERRIN, instead of $6,0 \cdot 10^{23}$), partly in consequence of inaccurate suppositions on b (e. g. $b=4m$), or formulae which do not hold without reservation, as e. g. that of the mean length of way, from which then s_0 was calculated (viz. $\pi N s_0^2 = v : l \sqrt{2}$).

For Argon a liquid density = 1,374 is found at -183° . From this follows for the molecular volume $(39,88 : 1,374) : 6 \cdot 10^{23} = 48,4 \cdot 10^{-24}$. As the molecules have not yet approached each other in this state to the shortest distance, we must assume that s_0 is smaller than the longitudinal dimension of the cubes, the volume of which amounts to the above value. Hence we have $s_0 < 3,64 \cdot 10^{-8}$.

We can also calculate s_0 from $\beta_0 = b_0 : v_k = 0,305$. As $v_k = 39,88 : 0,5308 = 75,13$, we get $b_0 = 0,305 \times 75,13 = 22,92$. The molecular

¹⁾ In (3) f was namely the factor of RT . Of course our considerations are only valid for not too low temperatures, as otherwise the limiting term RT must be replaced by the known more intricate form on account of the quanta effect. As, however, the *intra*-molecular vibrations will probably have a greater frequency than those of the molecules themselves, the temperature at which the influence of the effect in question will already make itself felt, will in general be higher than the corresponding temperature for the molecular system.

volume is therefore $38,2 \cdot 10^{-24}$. If in this shortest distance we still assume approximate cubic distribution¹⁾ of the molecules, then s_0 becomes $\geq 3,37 \cdot 10^{-8}$, which agrees very well with the just calculated upper limit²⁾.

We may therefore assume for argon $s_0 = 3,5 \cdot 10^{-8}$ cm.

PERRIN gives for this (Conseil Solvay, German edition, p. 154), the somewhat too low value $2,7 \cdot 10^{-8}$, calculated from the length of path.

For *Hydrogen* we find 0,086 (DEWAR) for the density at the melting point³⁾. Hence $s_0^3 < (2,0152 : 0,086) : 6 \cdot 10^{23}$, or $s_0^3 < 39,1 \cdot 10^{-24}$, $s_0 < 3,39 \cdot 10^{-8}$.

The value of b_0 at H_2 being only known by approximation, no lower limit can be given. The value of b_0 calculated by me before (These Proc. of April 24, 1903) by means of VAN DER WAALS' equation of state of the molecule is not suitable for this purpose. I found then namely b_g almost independent of the temperature, on the other hand b_0 increasing with T , which is not probable. If for b_g the value 0,000917, found before, is assumed, we find about 0,00076 for b_0 with $b_k : b_0 = 1,2$, hence $s_0^3 \geq (0,00076 \times 22412) : 6 \cdot 10^{23} \geq 28,3 \cdot 10^{-24}$, or $s_0 \geq 3,05 \cdot 10^{-8}$.

[We once more draw attention to this, that if we had put $b = 4m$ according to the current assumption, and $b_0 = \pm 2m$ according to the theory of the apparent diminution of b , we had found a much too small value for the lower limit].

For the present we can therefore assume $s_0 = \pm 3,2 \cdot 10^{-8}$ for H_2 .

The value $4 \cdot 10^{-8}$, calculated from unknown data, which I found given somewhere, is therefore slightly too great.

¹⁾ I. e. that even at the greatest density the molecules do not occupy a smaller volume than s_0^3 . Only on the supposition of perfect spherical form, and the entire lack of impenetrable spheres of influence (see § 1) could it be assumed that a smaller minimum volume than s_0^3 were possible. This, however, seems a physical impossibility to me, and — like the assumption of an apparent diminution of b in consequence of the partial overlapping of the distance spheres — only a mathematical fiction. Also the existence of crystal nets seems to plead strongly against the assumption of a denser accumulation than corresponds with s_0^3 . It might sooner lead us to the opposite conclusion.

²⁾ The sign of inequality $>$ namely refers to the *possibility* that the molecules can occupy a somewhat smaller volume than s_0^3 .

³⁾ To my regret I have no tabular works as the latest edition of LANDOLT und BÖRNSTEIN, *Recueil de constantes physiques*, and others at my disposal, so that I had to be content with this slightly antiquated value of DEWAR. I do not know any clear summary of the constants determined in the Leiden Laboratory for different substances. Neither in KAMERLINGH ONNES and KEESOM's book on the equation of state, nor in that of KUENEN did I find, except incidentally, numerical values of experimentally determined constants.

For *Helium* KAMERLINGH ONNES (Suppl. 21) has found $d = 0,15$ for liquid *He*. Hence $s_0^3 < (3,99 : 0,15) : 6 \cdot 10^{23}$, or $s_0^3 < 44,5 \cdot 10^{-24}$, therefore $s_0 < 3,54 \cdot 10^{-8}$.

If for b in the case of *He* the value 0,0007, given in Suppl. 21, is assumed, then b_0 is about $0,007 : 1,12 = 0,000625$, hence $s_0 \geq (0,000625 \times 22412) : 6 \cdot 10^{23}$, i.e. $\geq 23,35 \cdot 10^{-24}$, or $s_0 \geq 2,86 \cdot 10^{-8}$.

This value is evidently too small; perhaps the b -value, for which K. O. first (Comm. 102a) gave 0,00043, and which was later on raised to 0,0007, must be raised somewhat more.

We therefore assume for *He* the middle value $s_0 = \pm 3,2 \cdot 10^{-8}$.

PERRIN'S value, viz. $1,7 \cdot 10^{-8}$ (loc. cit.), is at any rate too low.

It appears from the above examples, that for three substances which differ so much as Argon (mol. weight = 40), Helium (mol. weight = 4) and the di-atomic H_2 (mol. weight 2), the values of s_0 differ very little.

Also on calculation of other not too complex substances s_0 appears to rise very rarely above $4 \cdot 10^{-8}$.

The found values are in better harmony than could be expected with the value $\pm 3,9 \cdot 10^{-8}$, which follows from our theoretical considerations. Not only is the order of magnitude the same, but even the numerical value is almost identical.

When we bear in mind that $s_0 \cdot (d : s_0)^3 = 3,9 \cdot 10^{-8}$, then $(d : s_0)^3 = 1,11$ would follow from e.g. $s_0 = 3,5 \cdot 10^{-8}$ (for Argon), hence $d : s_0 = 1,04$. The diameter of the molecule would therefore be a little smaller than the distance of equilibrium d of the two charges, which might point to a somewhat elongated form of the molecule, because then the mean diameter s_0 would be somewhat smaller than the distance of the centres, in which the charges may be imagined fictitiously concentrated. But though this supposition is very plausible, particularly for di-atomic gases, yet there is by no means certainty on this head on account of the not absolute accuracy of the calculated values. The more so as there may also be other influences at work, of which we only mention that of the degrees of freedom by which the factor f is influenced; and also the influence of the deviation from the law of equipartition, through which in (3) the factor f would apparently become smaller. But even when we leave the factor $(d : s_0)^3$ in (7a) out of account, the concordance between the value of s_0 , calculated from the assumption of electrical forces and the values found for different substances, in connection with VAN DER WAALS' equation of state of the molecule and the temperature coefficient of $(b_g - b_0) : b_0$ found by me, remains remarkably close.

Fontanivent sur Clarens, October 1914.