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Physics. — *"On* van der Waals' *equation of state,"* by Dr. Ph. Kohnstamm. (Communicated by Prof. van der Waals).

§ 1. The way, in which we have to take the extension of molecules into account for the derivation of the equation of state, has been repeatedly a subject of discussion. It is known that, in order to avoid the introduction of repulsive elastic forces and therefore the apparent contradiction with the supposition that only attractive forces act, van der Waals has, in the first derivation of his equation, not allowed for this extension by means of the virial, but by quite other means. This departure from the path first taken was disapproved of by Maxwell[1]), and strongly condemned by Tait[2]), who himself from the equation of the virial had arrived at an equation of state, as also Lorentz had derived, viz. :

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v}\left(1 + \frac{b}{v}\right) \quad . \quad , \quad . \quad . \quad . \quad . \quad (1)$$

More than ten years ago an interesting controversy was carried on between Tait[2]), Rayleigh[3]) and Korteweg[4]) on the value of this form in comparison with the original form :

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Whereas Tait considered an equation of the form (1) as the only correct one and the derivation of van der Waals as decidedly wrong, because it could never lead to this form, Korteweg thought that he could prove, that on the contrary the final result ought to have form (2), a form which he greatly preferred. This preference, which is not to be justified from a purely mathematical point of view as the two formulae are identical when we take only the terms of the order $\frac{b}{v}$ into account — and the terms of higher order are neglected in both cases — may be easily understood when we consider that we have here to do with physical problems. For whereas from the form (1) neither the existence of a minimum volume, nor

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1) Nature **10**, p. 477.

2) Nature **44**, p. 546, 627; **45**, 199.

3) Nature **44**, p. 499, 597; **45**, 80.

4) Nature **45**, p. 152, 277.

that of a critical point can be derived [1]), it is known that equation (2) indicates both, though not numerically accurate; one of the numerous cases, where the equation of van der Waals is a safe guide for the qualitative course of the phenomena, though it is unable to represent them quantitatively. Korteweg derives, therefore, from the equation (1), (2) [2]) by putting as it was deduced by van der Waals and himself $P = \dfrac{\sqrt{2\pi n s^2}}{v-b}$ for the value for the number of collisions

instead of $P = \dfrac{\sqrt{2\pi n s^2}}{v}$, which value was used by Tait and Lorentz.

This discussion has not led to a perfect agreement, any more than a later discussion carried on between Boltzmann [3]) and van der Waals [4]) about the corrections, which are to be applied to the value of b, which is put constant in (1) and (2) and equal to the fourfold of the volume of the molecules. As is known, Jäger [5]) and Boltzmann [6]) found by first approximation $b_v = b_\infty \left(1 + \dfrac{5}{8}\dfrac{b}{v}\right)$ for the b from (1);

van der Waals $b_v = b_\infty \left(1 - \dfrac{17}{3}\dfrac{b}{v}\right)$ for that from (2); afterwards

van der Waals Jr. [7]) has found for the latter $b_i = b_\alpha \left(1 - \dfrac{3}{8}\dfrac{b}{v}\right)$ in a different way, so that his result, as far as the terms of the order $\dfrac{b}{v}$ and $\dfrac{b^2}{v^2}$ are concerned, agrees with that of Jäger and Boltzmann. In his publications which have appeared since [8]), his father has pronounced himself "inclined to acknowledge $^7/_8$ as the correct value," but it is not doubtful for an attentive reader, that this "inclination" leaves ample room for doubt, both with regard to the value of the coefficient $^7/_8$, and to the following coefficient β, which was given on one side as 0.0958, on the other side as 0.0369.

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[1]) Evidently Tait has not seen this, but he thinks that the peculiarity of form (2) exists in this, that it is a cubic with respect to r; evidently on account of the part which the three sections of the isotherm with a line parallel to the r-axis, play in the theory of van der Waals But he overlooked, that every valid equation of state will have to represent these three volumes.

[2]) See also van der Waals: Continuität 1899, p. 60.

[3]) These Proc. I, p. 398.

[4]) These Proc. I, p. 468.

[5]) Wien. Sitzungsber. 105, p. 15.

[6]) Gastheorie, p. 152.

[7]) These Proc. 5, p. 487.

[8]) These Proc. 6, p. 135.

Now it has clearly appeared of late, of how preponderating an importance the knowledge of these corrections is for an accurate equation of state. In the first place Brinkman[1]) has succeeded in proving, that the behaviour of air at 0° between 1 and 3000 atms. can be very accurately represented by means of coefficients which do not differ considerably from the values found by Boltzmann; then van der Waals[2]) has proved — as van Laar[3]) had done before — that with the aid of these corrections the critical coefficient

becomes $\left(\dfrac{RT}{pv}\right)_c = 3.6$ and in this way one of the great discrepancies

between theory and experiment seems to be removed. And this last result makes it again clear, how great from a physical point of view, the difference is between an equation of form (1) and (2), though from a mathematical point of view they may be identical by first, second and further approximation. Already a long time ago Dieterici[4]) proved, as lately Happel[5]) has also done, that with an equation of the form:

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v}\left\{1 + \frac{b}{v} + a\frac{b^2}{v^2} + \ldots\right\} \quad \cdot \quad \cdot \quad (3)$$

the critical coefficient can reach at the utmost the value 3 with the theoretical values of the coefficients, and that this form can therefore never represent the experimental data. It seems therefore not devoid of interest to me, to examine the different derivations of the equation of state, in order to find which form must be taken as the correct one. This investigation will at the same time enable us to form an opinion about the difference between Boltzmann and van der Waals.

§ 2. As is well-known, the proof which van der Waals originally gave for his equation of state, rests on two theorems, the first of which is explicitly stated, the other is assumed without argument as self-evident. The first theorem states, that the number of collisions in a gas with spherical molecules is represented by the before-

mentioned formula $P = \dfrac{\sqrt{2\pi n s^2}}{v-b}$. Now I have already pointed out

in a former paper[6]), that this formula is inaccurate, and must

[1]) These Proc. VI, p. 510.

[2]) Boltzmann-Festschrift, p. 305.

[3]) Archives Teyler (2) VII.

[4]) Wied. 69, p. 685.

[5]) Drude 13, p. 352.

[6]) These Proc. p. 787.

be changed by first approximation into $P = \dfrac{\sqrt{2\pi}\,ns^2}{v}\cdot\dfrac{1-\dfrac{11}{8}\dfrac{b}{v}}{1-2\dfrac{b}{v}}$ or

neglecting the terms of higher order $P = \dfrac{\sqrt{2\pi}\,ns^2}{v}\left(1 + \dfrac{5}{8}\dfrac{b}{v}\right)$.

The other theorem says that the pressure on the wall (or an imaginary partition) is inversely proportionate to the mean length of path. Already KORTEWEG[1]) has felt an objection to this theorem, and has therefore looked for another way of deriving the equation of state; though convinced of the validity of the theorem, VAN DER WAALS[2]) has later on given another proof, because he considered this theorem as a not to be proved dictum. After the appearance of the already cited paper by VAN DER WAALS JR., however, it is in my opinion beyond doubt, that this theorem does not contain an unprovable truth, but — at least in the terms given here — a provable untruth. For it says the' same thing as the statement, that the pressure exerted by the collisions on the distance-spheres per plane unity is equal to that on an imaginary or real wall. It seems to me, however, that VAN DER WAALS JR. has convincingly proved, that when the terms of the order $\dfrac{b}{v}$ are taken into account, the relation between these pressures defined in the usual way, is $1 - \dfrac{3}{8}\dfrac{b}{v}$.

If this result is combined with the just mentioned value for the number of collisions, which determine the pressure on the distance-spheres, it is seen, that also in this way the fourfold of the volume of the molecules is found as first correction, but for the present this does not teach us anything about the final form, because in the communication of VAN DER WAALS JR. the relation of the pressures is not given in its true form, but developed to an infinitely extended series with neglect of the higher powers, which are, however, material to the determination of the final form.

In order to derive the final form, we may, if we want to avoid speaking of repulsive forces, make use of the method based on the increase of the transport of moment brought about by the collisions. We start in this from the observation, that the quantity of motion, which, bound to the molecules, generally moves on with the velocity of them, proceeds in a collision over a certain distance with infinite

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1) Verslagen der Kon. Ak. Afd. Natuurk. Tweede reeks, X, p. 362.
2) Continuität 1899, p. 60 cf.

velocity which is best seen by imagining a central shock, in which both molecules pursue their way in the direction from which they came, but adopting each other's motion. It is therefore just as if they have passed through each other with infinite velocity and as if further nothing has happened, so also as if the quantity of motion — of whose motion the pressure of the gas is a consequence — does not move with the velocity of the molecules, but as if with every mean path which is described, a distance is saved, which is a mean of the distances of the centres of the molecules in collisions. If the distance obtained in this way is $^1/_3\, s\sqrt{2}$ for every mean path of

$\dfrac{v}{\sqrt{2}\,\pi n s^2}$, then the increase of the pressure is:

$$\frac{\dfrac{v}{\sqrt{2}\,\pi n s^2} + {}^1/_3\, s\sqrt{2}}{\dfrac{v}{\sqrt{2}\,\pi n s^2}} = 1 + \frac{b}{v}$$

If the mean path. when we take into consideration that the distance spheres cover each other, is $\dfrac{v}{\sqrt{2}\,\pi n s^2}\beta$, where $\beta = \varphi\left(\dfrac{b}{v}\right)$, then the factor which we must take into account is $1 + \dfrac{b}{v}\beta$, and we get the strictly accurate equation:

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v}\left(1 + \frac{b}{v}\beta\right) \quad\ldots\ldots\ldots (4)$$

The train of thought which we have sketched here in a few words, and from which G. Jäger (loc. cit.) arrived for the first time at the correction term $b_v = b_\infty\left(1 + \dfrac{5}{8}\dfrac{b}{v}\right)$ has already been rigorously developed by Korteweg[1]), but he seems to have come to another result. This disagreement is, however, only seeming. Korteweg says[2]): "the sum of all the distances saved by collisions is therefore $4\,APv\cos\varepsilon\,dt$[3]). The sum, however, of all the distances with which the P molecules approach the plane AB in the time dt is evidently $Pv\cos\varepsilon\,dt$."

Now it is beyond doubt in my opinion, that if a number of molecules in the time dt by their own velocity pass over a way $Pv\cos\varepsilon\,dt$,

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[1]) Verslagen der Kon. Ak. Afd. Natuurk. Tweede reeks X p. 362.

[2]) l. c. p. 369.

[3]) $A = \dfrac{b}{4v}$ in our terminology; v represents the velocity of the molecules in Korteweg's paper.

and at the same time a way $4\,APv\,cos\,\varepsilon\,dt$ is saved by the collisions, those molecules seem to move with a velocity $Pv\,cos\,\varepsilon\,dt(1+4A)$, and so the number of collisions has increased in the same ratio. KORTEWEG, however, continues: "In order to obtain therefore the same number of collisions with the plane AB, the molecules will only have to pass over a way $Pv\,cos\,\varepsilon\,dt$, instead of over a way $Pv\,cos\,\varepsilon\,(1-4A)\,dt$, in other words, the number of collisions of this system increases in the ratio $(1-4A)\cdot1$." Now between the two results there is only difference of order $\dfrac{1}{A^2}$ and in so far as we wish to neglect the quantities of this order, KORTEWEG's result may certainly be accepted. If, however, we wish to solve the problem rigorously, the first result alone can be accepted.

For KORTEWEG makes it appear, as if — taking into account the part of the way being saved — an equally long way is described in the time $(1-4A)dt$, as in the time dt without doing so. Now in the last case the molecules pass over a way $Pv\,cos\,\varepsilon\,dt$ in the time dt, so $Pv\,cos\,\varepsilon\,dt\,(1-4A)$ in the time $(1-4A)dt$. In the time dt there is saved $4\,APv\,cos\,\varepsilon\,dt$, in the time $(1-4A)dt$ therefore $(1-4A)\,4\,APv\,cos\,\varepsilon\,dt$; so the distance, passed over in the time $(1-4A)dt$ by saving way and really moving together is somewhat slighter (viz. $16\,A^2Pv\,cos\,\varepsilon\,dt$) than that passed over by the real motion alone in the time dt[1]).

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[1]) Perhaps KORTEWEG was led when drawing up the formula mentioned in the text by the solution of the problem in one dimension which he has given in Nature (loc. cit.) later on. He finds there — perfectly accurately — for the time passing between two collisions against the wall of a row of n particles of diameter λ which can move over a total distance L with a velocity V:

$$T = \frac{V}{L-n\lambda}.$$

This formula reminds us more of KORTEWEG's result than of ours, really however it agrees with the latter, not with the former. For, if we determine the ratio of the number of collisions with and without saving way, it is $Q = \dfrac{L}{L-n\lambda}$. Now L is the total distance over which the molecules can move, so the path described by their own motion + the path saved; $n\lambda$ is the path saved. So L corresponds with $(1+4\,A)\,Pv\,cos\,\varepsilon\,dt$, $n\lambda$ with $4\,APv\,cos\,\varepsilon\,dt$; so the ratio of the collisions is here again $(1+4\,A):1$. To KORTEWEG's result $1:(1-4\,A)$ would the formula $Q = \dfrac{L-n\lambda}{L-2\,n\lambda}$ correspond, which agrees with the first as to the terms of the order $\dfrac{n\lambda}{L}$, but which is certainly not *strictly* accurate.

It is true that with the formula for one dimension, with regard to its physical meaning, an equation of state agrees, in which a quantity is subtracted from the volume which is a function of b and v, not a formula of form (1); but we shall see that our formula derived in the text, leads also to such a final form.

§ 3. So we arrive at equation (4) without making use of the equation of the virial and without speaking of repulsive forces. That the introduction of these and the determination of the so-called "repulsive virial" in the same way as has been done by Lorentz, Tait and Boltzmann, leads to the same result, is easy to see, if we put everywhere $\dfrac{\sqrt{2}\,\pi n s^2}{v}\,\beta$ instead of $\dfrac{\sqrt{2}\,\pi n s^2}{v}$ for the number of collisions in the formulae used by them. The expression β does not depend on any of the integrations and the repulsive virial yields therefore $RT\dfrac{b}{v}\beta$ instead of $RT\dfrac{b}{v}$. This is easy to understand, even without following the proofs of Lorentz and Boltzmann, for it is clear that the term which is introduced into the equation of the virial through the collisions, must be proportional to the number of those collisions, as two collisions can never be of a different kind [1]).

It seems therefore as if theory really leads to the form expected by Tait and Dieterici, which conforms so little with the experiment. In reality, however, the result is quite different. For — as I pointed out in my other communication — β has by first approximation not the form: $1 + \dfrac{5}{8}\dfrac{b}{v}$, as Jager and Boltzmann generally write, but we find in the way first indicated by Clausius $\dfrac{1 - \dfrac{11}{8}\dfrac{b}{v}}{1 - 2\dfrac{b}{v}}$ for it, and only by carrying out the division and by neglecting the terms of higher order, we get the form $1 + \dfrac{5}{8}\dfrac{b}{v}$. As I showed, we get, taking the terms of higher order into account:

$$\beta = \frac{1 - \dfrac{11}{8}\dfrac{b}{v} + B\dfrac{b^2}{v^2}\ldots + N\dfrac{b^n}{v^n}}{1 - 2\dfrac{b}{v} + \dfrac{17}{16}\dfrac{b^2}{v^2} + C_1\dfrac{b^3}{v^3}\ldots + N_1\dfrac{b^n}{v^n}} \quad\ldots\quad (5)$$

where n is a finite number.

Now it is true that the other coefficients of this series, C_1 and B excepted, are unknown, and we might conclude from this, that it must therefore be indifferent for the present, whether the equation of state is written

[1]) Korteweg and van der Waals have also made use of this property in their derivation of equation (2) from (1), mentioned on p. 795.

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v} \left\{ 1 + \frac{b - \frac{11}{8}\frac{b^2}{v} + B\frac{b^3}{v^2} + C\frac{b^4}{v^3}}{v - 2b + \frac{17}{16}\frac{b^2}{v} + C_1\frac{b^3}{v^2}} \right\} \quad . . \quad (6)$$

or

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v} \left\{ 1 + \frac{b}{v} + \frac{5}{8}\frac{b^2}{v^2} + \beta\frac{b^3}{v^3} \right\} . \quad . . . . \quad (7)$$

but this conclusion would be unjustifiable. For it is possible, nay even probable, that the coefficients of numerator and denominator in (6) decrease rapidly; it is therefore possible, that the true form is accurately represented by a quotient of two forms, which have each only three or four terms; from this follows by no means, that also in the form (7) we should get a close approximation with three or four terms, for the coefficients of the higher powers in (7) do not depend only on the coefficients of the *higher* powers in numerator and denominator of (6), but they are also functions of the coefficients of the lower powers 1; $^{11}/_{8}$; 2; $^{17}/_{16}$; and in such a way that they do not become zero, when the coefficients of the higher powers in (6) do so. Now the difference between (6) and (7) vanishes, of course, for such large values of v, that the series (7) converges strongly, but for the critical volume and even more so for liquid volumes the difference is very pronounced. This appears already from the simple fact, that a form as (6) can easily yield a minimum volume; but (7) only when an infinite number of terms is taken into account. And also the before mentioned difference between the results of DIETERICI on one side, and VAN LAAR and VAN DER WAALS on the other side, prove how careful we must be with the introduction of simplifications which seem perfectly allowable.

§ 4. Also the other ways proposed for finding the equation of state, arrive at similar final results.

This is easy to see for the most direct way, indicated by BOLTZMANN [1]. For it is clear, that his formula (4), which leads to the form:

$$\left(p + \frac{a}{v^2}\right)\frac{v - 2b}{1 - \frac{b}{v}} = RT \quad . . . . \quad (8)$$

requires another correction on account of the fact that the distance spheres cover each other partially. The numerator of this fraction

[1] Gastheorie p. 9.

becomes then identical with the denominator of the fraction from (5).
In the denominator we get a correction for the part of the cylindre
γ, which falls within more than one distance sphere, or as we may
also say, for the part of a surface A, which is found within more
than one distance sphere, if we define this surface A by the condi-
tion, that it is found everywhere at a distance s from the outer
surface. We shall call this surface A henceforth "surface of impact",
because the force which in a collision acts on the centres of the
molecules, acts in this surface. The determination of the numerical
value of the further coefficients seems an exceedingly elaborate work,
at least BOLTZMANN announced already in the LORENTZ volume of the
Arch. Néerl. that he would have this calculation carried out for the
next coefficient. but this calculation has not yet been published. It
seems, however not doubtful to me, that also the numerical value
must be the same as the value found in other ways. At all events
the final form becomes also by this method

$$\left(p + \frac{a}{v^2}\right)\left(\frac{v - 2b + \dfrac{17\,b^2}{16\,v} + \ldots N_1\,\dfrac{b^n}{v^{n-1}}}{1 - \dfrac{b}{v} + \beta\dfrac{b^2}{v^2} + \gamma\dfrac{b^3}{v^3} \ldots + v\dfrac{b^n}{v^n}}\right) = RT \quad . \quad . \text{ (9)}$$

in which n represents a finite number.

Now it is not difficult to show that the only remaining method
for deriving the equation of state, which led to the correction $^{17}/_{32}$,
must lead to exactly the same equation as (9), when its principles
are consistently applied. As is known, this method assumes, that
the pressure is to be integrated not only over the volume v, but
also over half of that of the distance spheres. b, because a molecule
whose centre has got on a distance sphere, is subjected to exactly
the same force as when it has got on the surface of impact (the
volume enclosed by the surface of impact may be put $= v$). The
volume of the distance spheres, however, is really smaller than b,
because some distance spheres coincide, and we get therefore [1])

$$\left(p + \frac{a}{v^2}\right)\left(v - b + \frac{17}{32}\frac{b^2}{v}\ldots.\right) = RT \quad . \quad . \quad . \text{ (10)}$$

Now VAN DER WAALS Jr. (loc. cit.) has already pointed out, that
it is tacitly assumed here, that the surface of the distance sphere
which is found within another distance sphere experiences a pressure
$= 0$, and that therefore, for the sake of consequence, also the parts of
the surface of impact falling within distance spheres, must be supposed

[1]) Continuität 1899, p. 65.

to experience a pressure $= 0$. He has, however, not worked out this thought further; as it seems to me, because he has not fully appreciated the ideas which led his father to the correction $^{17}/_{32}$. He has, therefore, substituted for this view, another, undoubtedly correct one, but he has not explained, how the former might be completed in order to yield also the true result. If, however, we make use of the observation made by him, then it is clear that the pressure which seems to be $P = p + \dfrac{a}{v^2}$ per unit of surface when we think it as working in the usual way on the total area of the surface of impact O, must be really larger in the gas, viz. equal to $p' = P \dfrac{O}{O'}$, when this pressure p' acts only on the *free* surface O'.

Now it is clear that this quantity $\dfrac{O}{O'}$, which hereby gets into the denominator of the first member of the equation of state is identical with the quantity introduced by Boltzmann in this place. For he, too, determines this denominator by examining what part of the surface of impact falls within the distance spheres. This shows us at the same time another point. In the few words which van der Waals[1] bestows on this derivation of the equation of state, he says, that the pressure is not to be integrated over the total volume of the distance spheres, as we might expect, but over half of it. Now I have been struck with this from the beginning, and I have tried to find the reason in vain. It appears from what precedes that we have really to integrate over the total volume and that van der Waals' has only introduced the division by two as compensation for the circumstance overlooked by him, but which we take here into account. So he got $v - b$, instead of $\dfrac{v - 2b}{v - b}$, which evidently does not make any difference by first approximation. But already the second approximation cannot properly be found in this way.

It appears now, that we must integrate the pressure p', determined in the way above indicated, over the whole outer surface, that of the distance spheres included in so far as they fall outside each other[2]), and that

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[1]) Continuität 1899, p. 62.

[2]) The logical inference from this theorem: that the true equation of state is found by assuming that every surface element, lying either on a plane or a curved wall, experiences a pressure: p' per unit of surface provided it does not lie within a distance sphere, in which case the pressure must be put equal to 0, would involve, that we did not integrate the pressure over the available volume (volume diminished by the free volume of the distance spheres), but that another correction was applied

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the axiom from which VAN DER WAALS started, viz. that we must equate the pressure on the distance spheres and that on the outer wall, is true, if only we apply it to the pressure p'. This result is only in apparent contradiction with the result of VAN DER WAALS JR., that the pressure P on a fixed plane wall stands to the pressure P' on the distance spheres in the ratio of $1 : 1 - \dfrac{3}{8}\dfrac{b}{v}$. For these pressures P and P' have been found by supposing the quantity of moment furnished by the wall (and the distance spheres) in the collisions to be distributed over the *total* surface, so by assuming that every surface element contributes an equal amount to the impulse; the pressure p' of which there is question here, and which proved to be the same for both, is found on the other hand by supposing, that only the mean *free* surface contributes to the quantity of motion, and that the rest is therefore subjected to a pressure $= 0$.

From this follows:

$$P = p' \frac{\text{free area of surface of impact}}{\text{total area of surface of impact}} = p'\left(1 - \frac{b}{v}\right)$$

$$P' = p' \frac{\text{free surface of distance spheres}}{\text{total surface of distance spheres}} = p'\left(1 - \frac{11}{8}\frac{b}{v}\right)$$

and so $\dfrac{P'}{P} = \dfrac{1 - \dfrac{11}{8}\dfrac{b}{v}}{1 - \dfrac{b}{v}} = 1 - \dfrac{3}{8}\dfrac{b}{v}$ with neglect of the terms of higher order.

The importance of the proof completed in this way, lies for me in the fact, that it makes use of the idea of systems of molecules whose intra-molecular forces need not be introduced into the equation of the virial, provided we adopt the pressure integrated over the whole volume of these systems in the virial. I need not point out the great advantages of such a point of view, already cursorily mentioned by VAN DER WAALS in his dissertation, and later worked out; the communications of VAN DER WAALS on the equation of state and the theory of cyclic motion are striking evidences of its value.

Now it is true that there is a difference between our case and the cases, to which this view is applied in the communications

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in connection with the volume of the distance spheres, which are cut by the surface of impact. This correction would come to an increase of the volume to be integrated with that part of the distance spheres that is found between the surface of impact and the outer wall, but it is clear that this volume may be neglected with the same right as the total volume enclosed by those two surfaces.

mentioned. For in the latter we suppose the existence of really permanent systems of atoms, whereas in our case two molecules whose distance spheres cover each other partially, and which are therefore thought as a system, remain only together for an exceedingly short time. But we see that we get to the right result by assuming, that also the part of the surface of impact lying within the distance spheres, is part of a "system", and that therefore the force exerted on it, does not count [1]). This result is a priori by no means improbable, for this part of the surface of impact has exactly the same essential property as the other parts of "systems" viz. of falling within distance spheres, whereas in the communications mentioned this hypothesis for the surface of impact was not necessary, because there the systems are characterized by other properties which do not distinguish the surface of impact viz. that it is part of the same system for a comparatively long time.

§ 5. The result obtained in the preceding §, enables us now to use also the first method of reasoning of VAN DER WAALS for the determination of the final form without making use of the virial. For we have seen that the pressure P on the wall, when the pressure on the distance spheres P' is determined by

$$\frac{P}{P'} = \frac{\frac{\text{free}}{\text{total}} \text{ area of surface of impact}}{\frac{\text{free}}{\text{total}} \text{ surface of distance spheres}} \quad \ldots \quad (10)$$

Now the pressure on the distance spheres is, as appears from CLAUSIUS' formula for the length of path, proportional to :

$$\frac{\frac{\text{free}}{\text{total}} \text{ surface of distance spheres}}{\text{available volume}}$$

so that we find from this for P :

$$P = f \frac{\frac{\text{free}}{\text{total}} \text{ area of the surface of impact}}{\text{available volume}}$$

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[1]) The real significance of the introduction of these systems may be expressed in this way, that we think the situation of one given moment as fixed, and take into account the systems of more than one distance sphere formed in this way. This removes also what is paradoxal in the supposition (see v. D. WAALS JR. loc. cit. p. 644) that the pressure is 0 in those places which have just experienced a collision or will soon experience one, viz. the points in the distance spheres. For in this fixed state those points are really exempted from collisions from all *other* molecules than those belonging to their system, and whose pressure may therefore be considered as an intra-molecular force.

The signification of f we find by equating the volume of the molecules to zero; it appears then, that $f = RT$, so that the equation of state becomes

$$P \frac{\text{available volume}}{\frac{\text{free}}{\text{total}} \text{ area of surface of impact}} = RT$$

identical with (9).

Equation (10) shows us at the same time, what is the physical significance of the quantities used by van der Waals Jr. in his proof with the aid of the virial. For he integrates the pressure P over the volume v, the pressure P' over the volume b, so that the equation of state becomes:

$$\left(p + \frac{a}{v^2} \right) \left(v - b \frac{\frac{\text{free}}{\text{total}} \text{ surface distance spheres}}{\frac{\text{free}}{\text{total}} \text{ area of surface of impact}} \right) = RT \quad . \, . \, (11)$$

which is, moreover, at once seen, when we read the cited paper attentively. (Specially p. 492).

Though it is not clear to me, why we must integrate here over half the volume of the distance spheres, I must acknowledge that the result — to which we can also get without the proof in question by simply putting the results (6) and (9) identical — is correct. For calculations formula (11) which agrees closest with the original form of van der Waals, may be of use. I had hoped that I should be able to use the formula obtained in this way for removing the remaining discrepancies between experiment and theory, at least partially, specially the great difference in the value of $\left(\frac{T}{p} \frac{dp}{dT} \right)_t$.

As yet these efforts have not met with the desired success, and it is obvious, that this will not be possible, before we know e.g. the numerator of (11) much more accurately than we do now. It is clear that this numerator in virtue of its physical signification, can never become zero for volumes larger than the minimum volume; now we know this numerator only in the shape $1 - \frac{11}{8} \frac{b}{v}$, an expression which becomes zero for very much larger volumes, nay even for the ordinary liquid volumes. For these volumes therefore the application of the correction $1 - \frac{11}{8} \frac{b}{v}$ will be injurious, instead of advantageous. Not before the mathematical form of two of the three quan-

tities : $\dfrac{\text{free}}{\text{total}}$ surface distance spheres; $\dfrac{\text{free}}{\text{total}}$ area of surface of impact;
available volume, is more accurately known, we shall be justified
in expecting better concordance of experiment and theory.

Physics. — *"Note on* SYDNEY YOUNG'S *law of distillation."* By
Miss J. REUDLER. (Communicated by Prof. J. D. VAN DER
WAALS).

Some time ago SYDNEY YOUNG gave a law of fractional distillation[1]),
which seems very strange at first sight. According to this law in
distillations with an efficient still, the weight of distillate coming over
below the middle point of the boiling temperatures of the components
would be almost equal to the weight of the most volatile component,
also when the separation is far from perfect. This concordance
would be so close, that YOUNG could even base a general law of
quantitative analysis on it, at least for substances whose boiling
points were not too near to each other. Now it seemed, however,
unlikely, that this law should always hold, quite independent of the
nature of the Tx-curves and of the composition of the mixture
from which we start. Therefore I have distilled some mixtures,
inter alia also with YOUNG'S evaporator still head.

I began with some of the examples chosen by YOUNG, and I found
really that they confirmed the law. Then I tried to determine the
limits of its validity by taking a mixture with very steep Tx-line,
so that I could closely examine, what happens, when the distillation
is broken off above or below the mean boiling point. I took for
this benzene (boiling point 79°,6) and aniline (boiling point 180°)
and began with such a composition, that the initial boiling point
lay already above the middle point, thinking that YOUNG'S law would
be sure not to hold in this case. Yet also now the law was confirmed,
but the process of the distillation revealed also the character of the rule.
For it appeared that independent of the composition of the mixture,
even when it consisted of 4 °/₀ benzene and 96 °/₀ aniline, and so
a thermometer, which I had placed in the liquid, pointed to almost
180° already in the beginning of the distillation, the temperature in
the still head remained constant at 79° for a long time, and rose
then suddenly very rapidly to 180°, so that the distillation might
have been broken off with the same result very far above and

[1]) J. Chem. Soc. **81** 752.