The observations were made in the second order spectrum of a large ROWLAND grating.

The red of the second order is superposed on the blue of the third order so that the line 6708 is seen in the absorption spectrum as a blue line. With small vapour density the line resolved into two components; this proves that the conclusion drawn from the analogy of the spectrum series of the alkali metals is true. That component of the double line which has the smaller wavelength seemed to be the most intense. The distance between the components could only be measured in a roundabout manner by means of a divided scale in the eye piece of the spectroscope. This measurement gave for the distance between the components about one fourth of an Ångström unit. From the empirical rule that in the case of the elements of the same family the frequency differences of the pairs are nearly proportional to the square of the atomic weights, it would follow that for lithium this distance ought to be $6 \times \frac{7^2}{23^2} = 0{,}6$ Ångström units. The observed distance is much smaller.

Physics. — *"Some remarks on the course of the variability of the quantity b of the equation of state."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 25, 1913).

In my preceding communications I came to the conclusion that the differences which occur in the normal, not really associating, substances are to be ascribed to the different value of the quantity $\frac{b_g}{b_{lim}}$. As this quantity is greater, both f and s are greater, viz. $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$ and $s = \frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$. The deviation exhibited by the law of corresponding states, is also a consequence of the different course of the quantity b. Thus it becomes more and more clear that everything that can contribute to elucidate the cause of the difference in this course must be considered of the highest importance.

If the course of b is traced as function of v, a line is obtained which runs almost parallel to the v-axis with great value of v, and approaches asymptotically to a line parallel to the v-axis at a distance b_g from the latter. Not before $v = 2b_g$ does an appreciable difference begin to appear, and has the value of b descended to e.g. about

0,96 b_g. On further decrease of the volume b descends more rapidly — and when also a line has been drawn which starts from the origin, so from $v = 0$ at an angle of 45° to the v-axis, the continually descending b curve will meet this line at $b = b_{lim}$. If b_g and b_{lim} are given, this curve is determined. If b_g should have the same value, and if b_{lim} should be smaller, the curve lies lower throughout its course, and reversely if b_{lim} is greater, the whole b curve lies higher.

Of course if there did not exist a similar cause for the variability of b, we might imagine a more irregular course in the different b curves. But if such a cause is assumed, nobody will doubt of the truth of the above remarks. I have even thought I might suppose that there is a certain kind of correspondence possible in the course of the different b curves. The points of these curves which are of importance for the equation of state, run from $v = b_{lim}$ to $v = \infty$. At a value of $v = nb_{lim}$ (and n can have all values between 1 and ∞), $b_g - b$ is smaller as $b_g - b_{lim}$ is smaller. Now I deemed it probable that there would be proportionality between these two latter quantities, and that therefore the following character of these curves can be put, viz.

$$\frac{b_g - b}{b_g - b_{lim}} = f\left(\frac{v}{v_{lim}}\right),$$

and that this function of $\frac{v}{v_{lim}}$ is the same, entirely or almost entirely. When I considered the question what the meaning of this equation might be, the following thought occurred to me. Could possibly the quasi-association be the cause of this variability of b with the volume?

I treated this quasi-association in an address to the Academy in 1906, and later on in some communications in 1910, and I came then to the conclusion that it must be derived from the increase of tension of the saturate vapour in the neighbourhood of the critical temperature that at every temperature and in every volume a so-called homogeneous phase is not really homogeneous; but that dependent on the size of the volume and also on the temperature there are always aggregations of a comparatively large number of molecules which spread uniformly. In very large volume the number of these aggregations is vanishingly small and with small volume, and especially at low temperature this number increases greatly; so that at the limiting volume the number of free molecules has become vanishing small. If in each of these aggregations the value of b does not differ much from b_{lim} or perhaps coincides with it, the following value of

b might be derived. For that part of the substance that is in the state of free molecules the value of b is equal to b_g. If the fraction of the quantity of substance that is in the state of aggregation is put equal to x, and the fraction which is in the state of single molecules equal to $1 - x$, then $b = (1 - x)\ b_g + b_{lim}$ or

$$\frac{b_g - b}{b_g - b_{lim}} = x\,.$$

And if we compare this result with the equation the significance of which we tried to find, we see that $f\left(\frac{v}{v_{lim}}\right)$ is the function which determines the value of x in every volume, but we must at once add at any temperature. That b might also depend on T I have never denied; I have only denied that putting $b = f(T)$ would enable us to account for the course of the equation of state, but that chiefly the dependence of v is indispensable. So we should now have arrived at the relation:

$$\frac{b_g - b}{b_g - b_{lim}} = x = f\left(\frac{v}{v_{lim}}\,,\ T\right).$$

But I must not be detained too long by these considerations, for on further consideration I have had to reject the thought that quasi-association has influence in this way. For various reasons. First of all because at so great contraction of the volume the name of quasi-association would have to change into real association. Secondly because the generated heat would then have to be much more considerable — and further the course of association would also have to be different for almost complete association, to which I may possibly have occasion later on to draw the attention. This, however, obviates the necessity of making $\frac{b_g - b}{b_g - b_{lim}}$ dependent on T, and we return to the simpler equation:

$$\frac{b_g - b}{b_g - b_{lim}} = f\left(\frac{v}{v_{lim}}\right).$$

And though I am not yet able to give the theoretical form of this function, and though I cannot indicate a priori the constants occurring in it, I can apply a correction in the value of v_{lim}, which I gave in my least communication; and this has greatly weakened if not removed the objections I had to the assumption that the decrease of b with the volume is only an apparent explanation.

I have arrived at the value of $v_{lim} = b_{lim}$ by following the same train of reasoning as when I drew up the equation of state. For

the only new thought about the influence of the dimensions of the molecule (Chapter VI) was this that the volume inside which the motion of the molecules takes place, must be considered as in reality smaller than it seems at first sight.

If in case the molecules should be material points, the consequence of the collisions is that they resist an external pressure $+\frac{RT}{v}$, the consequence of their own dimensions is that they resist a pressure $\frac{v}{v-b}$ times as great. And we cannot dispense with this consideration. We may introduce this thought immediately, and without having to speak of repulsive forces, write directly: $p+\frac{a}{v^2}=\frac{RT}{v-b}$, or if it is preferred first continue the course of the calculation with the aid of the theorem of the *virial* further than I have done. But finally to arrive at the true formula it is again necessary to follow the course taken by me. I showed this long ago. When I wanted to determine the value of this new quantity b, however, I soon perceived that this would be attended with great difficulties.

It was not so difficult to determine the value of b_q, and I could at once conclude that b_q is equal to 4 times the volume of the molecules. And it was also easy to see that b would have to decrease with the volume. Already the consideration that for infinitely large pressure the volume would have to be smaller than 4 times the volume of the molecules, and would have to depend on the grouping in that smallest volume, and that therefore b_{lim} would have to be $< b_q$, was sufficient for this. In reference to this I say what follows in Chapter VI (p. 52), after I had reduced the way to determine the quantity b to the abbreviation of the mean length of path, and had therefore put:

$$\frac{l-l_1}{l}=\frac{v}{v-4l_1}:$$

"but this formula cannot be applied up to the extreme limit of condensation of the substance", etc. as far as the word "verwachten".

It appears from the cited passage that I felt already then that the quantity b in a definite volume would have to be determined by the determination of the distance, at which during the impact the centre of the colliding molecule must remain from the central plane at right angles to the direction of motion, in consequence of the dimension of the two colliding molecules. This appears among others when I say that when $v < 4b_1$ not only the double-central shocks,

but also the double tangent ones will not take place, and the factor 4 will not diminish so rapidly as might have been expected without taking this in consideration.

To make clear what I mean, imagine a molecule in motion to strike against another. On the supposition of spherical molecules draw a sphere which has its centre in the second molecule with a radius $= 2r$ (if r is the radius of a molecule). Then at the moment of the impact the centre of the colliding molecule must lie on that sphere with a radius twice as long as its own. Now imagine also through the second molecule a central plane at right angles to the direction of the relative motion, in which case the second molecule may be taken as stationary, then the mean abbreviation of the free length of path is the length of the mean distance at which the centre of the moving molecule lies from the said central plane. In very large volume the chance that the centre of the moving molecule strikes against a certain area of the sphere with $2r$ as radius is proportional to the extension of the projection of this area on the said central plane. It follows from this that the mean abbreviation of the free length of path is the mean ordinate of a half sphere with $4\pi r^2$ as basis, and so equal to $\frac{4r}{3}$. It is true that this is the abbreviation of the length of path for 2 molecules, but this is compensated by the fact that an abbreviation of the same value exists also at the beginning of the free length of path for the moving molecule.

If also in a small volume the chance to a collision with the sphere with $2r$ as radius could be determined, the way had been found to determine the value of b in every volume. For $v < 4b$ the double central impacts must be eliminated, but also the double tangent ones. And strictly speaking in every volume, however great, if not infinitely great, the chance to double central and double tangent impacts must have lessened. Here a course seems indicated to me which might possibly lead to the determination of the value of b for arbitrary volume. I do not know yet whether this will succeed, but at any rate it has appeared to me that this may serve to calculate b_{lim} and not only for spherical molecules. The latter is certainly not devoid of importance, as the case of really spherical molecules will only seldom occur.

Let me first demonstrate this for spherical molecules. In the extreme case when they are stationary, they lie piled up, as is the case with heaps of cannon balls, each resting on three others. Let us think the centres of these three molecules as forming the tops of the ground

plane of a regular tetrahedron. For a volume infinitely little greater than the limiting volume the limiting direction of the motion of the 4th molecule is that which is directed at right angles to the ground plane, and in case of collision the three molecules of the ground plane are struck at the same time. The sides of the tetrahedron have a length equal to $2r$, and the perpendicular from the top dropped on the ground-plane is equal to $2r\sqrt{\frac{2}{3}}$.

The abbreviation of the length of path in consequence of the dimensions of the molecules is equal to half $2r\sqrt{\frac{2}{3}}$, if one wants to make this comparable with the above found one of $\frac{4}{3}r$, because this value referred to the abbreviation at a collision of two molecules, whereas the now found abbreviation holds for a collision of 4 molecules. The number of times that $\frac{4}{3}r$ is greater than $r\sqrt{\frac{2}{3}}$, is the value of $\frac{b_q}{b_{lim}}$, or $\frac{b_q}{b_{lim}}$ is equal to

$$\frac{4}{3}\sqrt{\frac{3}{2}}=\sqrt{\frac{8}{3}}=1.633.$$

For spherical molecules, therefore, $\frac{f-1}{3}=1.633$ or f almost equal to 5,9 and $s=\frac{8}{3}\sqrt{1,633}$ or about 3,3. And then it would follow that these values $f=5,9$ and $s=3,3$ must be considered as the smallest possible values.

But I do not lay claim to perfect accuracy for these values. Doubts and objections may be raised against these results, which I cannot entirely remove. Hence the above is only proposed as an attempt to calculate b_{lim} for spherical molecules. The first objection is this — and at first sight this objection seems conclusive. The value of b_{lim} must be equal to v_{lim}. Is the thus calculated value of b_{lim} then the smallest volume in which stationary molecules can be contained? This is certainly not the case. The volume of n^3 stationary spheres placed together as closely as possible is equal to $4n^3r^2\sqrt{2}$ if n is very great, and accordingly $\sqrt{2}$ times smaller than if they should be placed so that every molecule would require a cube as volume with $2r$ as side. If this value must be the value represented by b_{lim},

$\frac{b_g}{b_{lim}} = \frac{4\frac{4}{3}\pi r^3}{4r^3\sqrt{2}} = \frac{2\pi\sqrt{2}}{3}$, and so in connection with the law given by me $f-1$ and s^2 would become much greater than the value given for them by experiment.

But the thus calculated value for stationary molecules is not what I have represented by b_{lim}; I should prefer to represent it by b_0. At the point where the b-curve meets the line which divides the angle between the v-axis and the b-axis into two equal parts, need not and cannot be the point in which b is equal to b_0. The b-curve does not cease to exist in this point; it passes on to smaller volume, or possibly follows the line $v = b$.

On closer consideration the b-curve appears to touch the line $v = b$ and at smaller volumes than that of the point of contact the value of v appears to be again larger than b.

In the same way as kinetical considerations were required for the determination of the value of b_g to show that b_g is equal to four times the volume of the molecules, and so equal to $4\frac{4}{3}\pi r^2 N$, b_{lim} cannot be found without the aid of kinetical considerations. And the attempt which I make to calculate the value of b_{lim}, follows the same train of reasoning as has been efficient for the determination of b_g. This train of reasoning is as follows. If the mean length of path for molecules without dimension is equal to $\frac{v}{N\,4\,\pi\,r^2}$, and if the abbreviation amounts to βr, then $\frac{v}{v-b} = \frac{v}{v - N\,4\pi\,r^2\,\beta r}$, or $b = \beta 4\pi r^3$.

For b_g is $\beta = \frac{3}{4}$, and if the above given calculation is correct, the value of $\beta = \sqrt{\frac{2}{3}}$ for b_{lim}. So that, if we also introduce a value $v_0 = b_0$, $\frac{v_{lim}}{v_0}$ amounts to $= 1{,}814$. If we assume a regular arrangement of the molecules in v_0 and v_{lim}, the distances of the centres are not equal to $2r$ in v_{lim}, but equal to $2r\sqrt[3]{1{,}814} = 1{,}22$ times $2r$.

But for moving molecules such a regular arrangement is perfectly improbable. For them no other rule is valid but this that within a certain small space of time in equal parts of the volume, if not in contact with the walls, the mean number of molecules is the same. But their arrangement in such an equal part of the volume is

entirely arbitrary and always varying. A regular arrangement as would be the case for cubic distribution, when in every molecule, 3 directions could be pointed out at right angles to each other according to which they would be surrounded by 6 neighbouring molecules placed at equal distances, while in all the molecules these three directions and distances would be the same, is altogether inconceivable. This is a fortiori the case with the other mentioned regular arrangements, according to which it would be possible in every molecule to point out several directions inclosing angles of 60°, according to which they are surrounded by other molecules. This would only not be absurd for stationary molecules, and then v_0 is not equal to b_0, but $v_0 > b_0$. Now it might appear that the b_{lim} introduced by me would really have to be b_0. I introduced the b_{lim} when I discussed the ratio of the greatest liquid density to the critical density, and made use for this purpose of the rule of the rectilinear diameter. This greatest liquid density occurs for $T = 0$, and would therefore seem to hold for stationary molecules. This, however, is only seemingly in my opinion. Below T equal e.g. to $\frac{1}{2}$ or $\frac{1}{3}$ T_k this rule cannot be verified, but apart from its approximative character this rule is extrapolated. It is then taken for granted that what we have observed over a wide range of temperature, will also hold outside these limits. And I too have assumed this in the determination of v_{lim}. All this refers to a volume in which moving molecules occur. And so, if we put $\frac{v_k}{v_{lim}} = 2(1+\gamma)$, the value b_{lim} in the relation of $\frac{v_k}{v_{lim}} = 2(1+\gamma) = r\frac{b_g}{b_{lim}}$ is also that which holds for moving molecules. If observations could also be made at $T = 0$, the volumes which are smaller than that in which the curve touches the line $v = b$, could be realized. And I do not doubt at all that in the immediate neighbourhood of $T = 0$ the rule of the rectilinear diameter would entirely fail.

Let us summarize the foregoing. There is only one point in which the b-curve has a point in which $v = b$. This takes place at a value of b which we have called b_{lim}, and in which, because $v = b$, the value of the pressure is infinitely great. In this point $\frac{db}{dv} = 1$. Then in:

$$\frac{-\frac{dp}{dv} - \frac{2a}{v^3}}{p + \frac{a}{v^2}} = \frac{1 - \frac{db}{dv}}{v - b},$$

because p and $-\frac{dp}{dv} =$ infinite, also

$$\frac{-\frac{dp}{dv}}{p} = \frac{0}{0} = \frac{\infty}{\infty}.$$

And the determination of v_{lim} and b_{lim} takes place as follows. In the formula yielded by kinetical considerations, viz.

$$\frac{v-b}{v} = \frac{v-4\pi r^2 \beta r}{v}$$

v_{lim} must be $= 4\pi r^2 \beta r$. And for the determination of v_{lim} the smallest value for β will have to be found. For collisions with 1-molecule at a time, $\beta = \frac{4}{3}$. For collisions with 2 molecules at the same time, so that at the impact 3 molecules are in contact, $\beta = \frac{2}{3}\sqrt{3}$. For collisions with 3 molecules at the same time, the value of β is equal to $\sqrt{\frac{2}{3}}$, as we saw above. And collisions with a greater number which are in contact at the same time, are excluded. So that now the value of $\frac{b_g}{b_{lim}} = \frac{4}{3}\sqrt{\frac{3}{2}} = \sqrt{\frac{8}{3}}$ for spherical molecules has been found back, but now on better grounds than above.

But this does not terminate the investigation into the value of b_{lim}. I have put the chance that in v_{lim} collisions with a single molecule or with 2 molecules might take place equal absolutely to 0. By putting $v_{lim} = 4\pi r^2 \beta r$ I have assumed the possibility that there is also a chance of collision for points the projection of which on the central plane at right angles to the direction of motion lies at the edge of this central plane, also still at this great density. A more complete investigation would probably yield a still somewhat lower value of β.

My principal aim was to draw attention to the difference in the value of b_0 and b_{lim}. I had been astonished myself at the comparatively small value of $\frac{b_g}{b_{lim}}$, whereas $\frac{b_g}{b_0}$ has such a large ratio. For spherical molecules the latter amounts to $\frac{4\pi}{3\sqrt{2}}$ or almost 3, whereas $\frac{b_g}{b_{lim}}$ may possibly come near to half 3. The relations at which I had arrived, viz. $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$ and $s = \frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$ would be altogether incorrect, if

one should confuse b_{lim} and b_0. It is, however, very easy to see that the pressure equal to infinitely great *can* occur when $v = b$, but that this is not the case for $b = b_0$. Then for spherical molecules $\frac{v_0}{b_0} = \frac{3\sqrt{2}}{\pi}$. And so the final point of the b-curve does not lie in the line which divides the angle between the v- and the b axes into two equal parts, but in the line which makes a much smaller angle with the v-axis, the tangent of which is about equal to $\frac{1}{\sqrt{2}}$ or about 0,74.

I have questioned myself whether I can account for the result at which I have arrived. Especially the existence of b_{lim} and the relation of this quantity to the existence of groups of molecutes which simultaneously, four at a time, collide, or at any rate are so close together that the space between them may be considered as zero. And though there are still numerous questions to which the answer cannot yet be given, and there is therefore reason to hesitate before publishing the foregoing, yet the considerations which result from this question have given me the courage which might else have failed me.

How large is the space allowed to the motion for molecules with dimension? The external volume must be diminished 1 by a volume at the wall. The centres of the molecules cannot reach the wall, but must remain at a distance $= r$. Hence if O is the area of the wall, a volume $= Or$ must be subtracted from the motion. 2. the centres cannot reach the surface of the molecules, but must remain at a distance $= r$. Then a volume $= O'r$ would have to be deducted, if O' is the area of the joint molecules, and so it would be the same thing if the molecules had a radius $= 2r$. But then if the molecule A collides with the molecule B, we have counted the space that is to be deducted, twice, both for A and for B. Of course the space to be deducted mentioned under 2 greatly preponderates on account of the great number of molecules.

But the occurrence of collisions is a reason for b_0 to be diminished. If a molecule strikes against the wall or if a molecule approaches the wall so closely that there is no room for another to pass, two parts of the space inaccessible to the motion overlap, and hence the extent of the inaccessible space diminishes. This is also applicable for the collisions of the molecules inter se. If two molecules are so close together that a third cannot pass between, part of the space which is inaccessible to the 3rd molecule overlaps, and b is diminished. The greater the number of collisions, so the smaller the volume, the more b is diminished. Whether also the temperature has influence

on this diminution of b has not yet been decided. In case of greater velocity there are indeed, more collisions, but we may also assume that they are of shorter duration. At the moment, however, I shall leave this point undecided. What I have said here about the cause of the diminution of b with smaller v is practically what I had assumed as cause already before when I assumed the so-called overlapping of the distance spheres as cause.

The formula then derived for $b = b_g - \alpha \frac{b_g}{v} + \beta \left(\frac{b_g}{v}\right)$ etc. was not satisfactory, and gave a far too rapid decrease with the calculated coefficients α and β. And the cause of this at least I think I shall have to attribute to the quasi association. If for a moment I disregard the motion, and think all the molecules to be distributed in pairs, every pair being in contact, the diminution in the value of b is $\frac{1}{2}$ N-times the overlapping of the space at the collision between these molecules. But if in the motion I again admit the arbitrary pretty regular distribution and if I assume the original space, the diminution in b would of course be much less, and would only hold for those that collide. So for every kind of collision either of 2 or 3 or 4 or perhaps of a greater number the chance that such a collision occurs in the given volume must be calculated, and this fraction must be multiplied by the parts of the spaces which overlap at every kind of collision.

In the formula $\frac{b_g - b}{b_g} = \alpha \frac{b_g}{v} + \beta \left(\frac{b_g}{v}\right)^2$ etc. $\frac{b_g}{v}$ represents the chance that 2 molecules come near enough to each other to bring about overlapping of the distance spheres; in the same way $\left(\frac{b_g}{v}\right)^2$ the chance that 3 distance spheres overlap etc. And multiplied by a certain coefficient this would also be the case in complete absence of any cause of association, so if there are no special reasons for the molecules to aggregate. The quantities α, β, are the pieces of the distance spheres that overlap. For b_g all the molecules without exception are counted, whether they are separate or whether they are part of an aggregation — and for the factor of α all the groups of 2 molecules, whether or no they appertain to a larger aggregation. But I have not yet calculated all this.

That with diminution of the volume the decrease of b will take place more and more rapidly may already be inferred from this that the number of every kind of collision or rather sufficient approach to each other, increases in a heightened degree, and at last if only the volume has become small enough, it may be assumed

that overlapping of the distance spheres takes permanently place. For an arbitrary direction of motion we shall probably not have to go any higher than to a sufficient approach of 4 molecules, and this would justify the above given calculation of $v_{lim} = b_{lim}$. We should have calculated this point when with decrease of v, the decrease of b is equal to it. Then $\frac{db}{dv} = 1$. With values of $v < v_{lim}$ all the molecules are not yet in contact; then there are still motions possible in this space, e. g. flowing of the substance or vibratory motions. But the motion which we call heat, has become impossible. Not until v_0 is reached does every motion become impossible The points of the b-curve, which I have continued as far as in b_0 above, have of course, no physical significance. The portion of the b-curve between $b_{lim} = b_0$ is then only to be considered as a parasitical branch. In the formula for the calculation of b this branch is probably also included. Accordingly I have entirely returned to the idea that the diminution of b is an apparent diminution of the volume of the molecules.

In these remarks I have touched upon several points which are of importance for the theoretical treatment of exceedingly condensed substances — without being able as yet to bring the investigation to a close. That I mention them already now is because I hope it may stimulate others to give their attention to it, and that they may try their strength to bring the investigation to a close. The determination of v_{lim} seems to me of special importance.

Summary of the results obtained in this and previous communications.

If it was rigorously valid the law of the corresponding states would have taught that all substances belonged to the same genus. This has proved not to be entirely complete. Experience teaches that from this point of view, there are differences. All the substances, indeed, belong to the same genus, but there are different species. If the quantities characteristic of a substance are called the quantities f, s, and r, they appear to differ. But these differences need not be considered as differences in 3 characteristic quantities, but they may be reduced to a single quantity. If this single quantity is called h, then $\frac{f-1}{1} = h$, $s = \frac{8}{3}\sqrt{h}$ and 2 is at least approximately equal to $\frac{3}{\sqrt{h}}$. When we try to find the significance of this characteristic quantity, it will be found, as was à priori to be expected in what was left out of account in the derivation of the law of corresponding

states, viz. the variability of b. This variability of b differs for different substances, and depends on the form of the molecules or on the quasi-association, which indirectly influences the course of b. If we put b_g for the greatest value of b and b_{lim} for the smallest value which is of importance for the equation of state, the ratio $\frac{b_g}{b_{lim}}$ is different. This ratio however, oscillates comparatively little round the value 2.

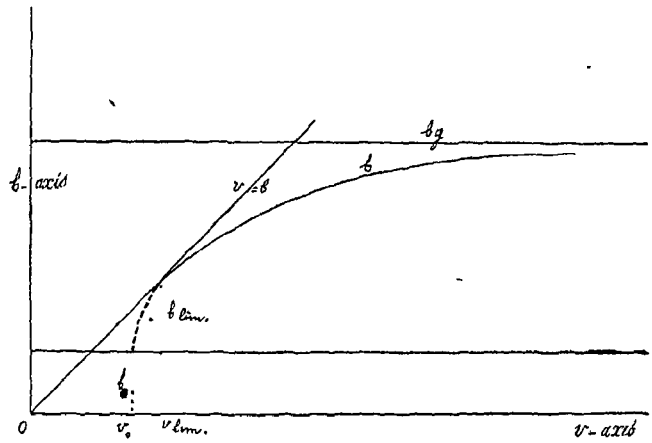

Fig. 1.

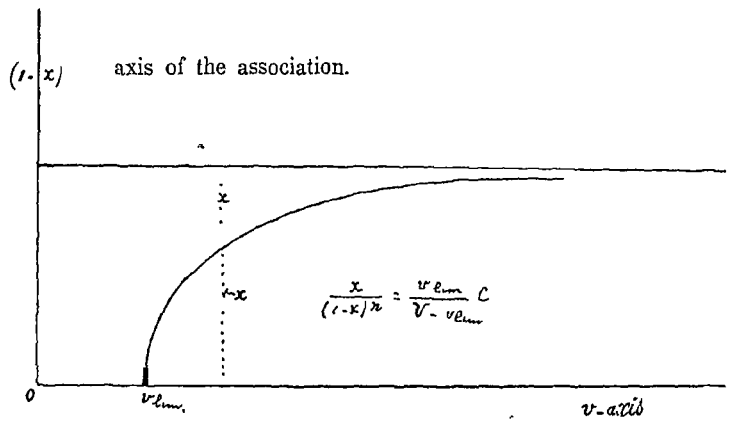

Fig. 2.

This ratio $h = \frac{b_g}{b_{lim}}$ determines, if I continue to speak of species, the species to which the substance belongs.

The value of b_{lim} is that value of b, for which v has the same value as b, and the pressure is therefore infinitely high. This value of $v_{lim} = b_{lim}$ is the smallest volume in which the substance can still be in thermal motion, but it is still appreciably greater than the joint volume, in which the molecules, when they were stationary, could be contained. The reduced equation of state which has the form

$$f\{\pi, v, m\} = 0,$$

if b should be put constant, assumes the form:

$$f\left\{\pi, \frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}, m\right\} = 0,$$

when the variability of b is taken into account, with gradually increasing deviation, however, as the density approaches the limiting density.

The form of this latter function is:

$$\left\{\pi + 3\frac{\frac{b_g}{b_{lim}}}{v^2}\right\}\left\{3\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}} - \frac{8}{rs}\frac{b}{b_g}\right\} = 8m.$$

The deviation gradually increasing with the density is caused by the variable term $\frac{b}{b_g}$. The influence of this deviation may be neglected for large values of v. At the critical density the different values of $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ differ only a few percentages. At the limiting density the value of this latter quantity is equal to $\frac{1}{f-1}$. Now that f oscillates round 7, this greatest difference is after all perhaps less great than might be feared, but yet not negligible, and manifests itself in the different directions of the rectilinear diameter [1]).

[1]) For more accurate and more definite views arrived at later I must refer to my "Weiteres zur Zustandsgleichung" Akademische Verlagsgesellschaft Leipzig, which will shortly appear.