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phenomenon which is common knowledge now-a-days (and which is mentioned even in elementary textbooks) was given by me 15 years ago¹⁾ and that I myself and my collaborators made use of it in our recent researches on the allotropy of bismuth, cadmium, copper and zinc.

The quotation reproduced above is so striking that discussion of the other instances of the same kind is unnecessary.

I have always intended to abstain from any remarks on this point. But as many colleagues both at home and abroad have taken increasing umbrage at the procedure of Mr. A. SMITS, I feel myself reluctantly compelled to draw attention to the matter.

Utrecht, VAN 'T HOFF-Laboratory.
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Physics. — “*A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour.*”
By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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

1. In my latest paper²⁾ I have treated some relations — also derived by VAN DER WAALS — in which a perfectly accurate form was substituted for the approximate one; I have proved that not any factor $\theta = f(v)$ by the side of a/v^2 , so not the factor $(1 - 1/2v)^2$, added to it on account of the so-called quasi-association either, is able to account for the course of the function $\varphi = \frac{f-1}{f_k-1} \cdot \frac{\varepsilon_{\text{coex.}}}{d_1 d_2}$ in the neighbourhood of the critical temperature (§ 3); I think I have demonstrated that either a , or b , or both must be functions of the temperature (§ 4), and I have made a few more remarks about the form of the reduced equation of state (§ 5). Now I wish to make some remarks on the form of the dependence of the quantity b of the volume v .

The temperature dependence will be considered in a subsequent paper. I may, however, state already now that I have come to the conclusion that this dependence too must be exclusively looked for in b , whereas a is assumed to be independent of the temperature. VAN DER WAALS seems finally also to have come to this conclusion, at

¹⁾ Zeitschr. f. physik. Chem. **30**, 623 (1899).

²⁾ These Proc. of Sept. 3, 1913, p. 44—59.

least I infer from an abstract in the Chem. Weekblad of Jan. 3, 1914, p. 29 of his most recent publication "Weiteres zur Zustandsgleichung" (summary of his latest Papers in these Proceedings of Nov. and Dec. 1912, Jan. and Febr. 1913), that he has adopted this opinion.

Thus the quantity b would control the whole thermic behaviour of the different substances, and the variability of this quantity in dependence on v , and also on T would be the cause that this actual behaviour deviates from that which would conform to VAN DER WAALS' *ideal* equation of state with a and b constant.

Further it seems to appear more and more that all the causes devised up to now, which were to account for the variability of b , yet jointly find their expression in one comparatively simple equation.

When the former supposition of perfectly hard and elastic spheres is abandoned for that of a *gradual* exchange of the energy during the collisions, in which at bottom the kinetic-energy of the moving and colliding molecules may be thought transferred to the interjacent medium, which transition determines the external pressure — part of the foundation of the before assumed correction on account of *apparent diminution* is no longer valid; at least in its old form.

When the molecules are considered as pretty stable systems, the volume of which varies only slightly in consequence of the increase of the internal and the external pressure, a great part of the correction introduced later on account of the *real diminution*, must no longer be applied. We are led to this view when we consider how exceedingly slight the influence of the temperature is *just at higher temperatures* (we shall come back to this presently), so that it seems that the molecule systems are only slightly modified in volume even by the influence of the thermal motion (which will certainly be more intense than that of the pressure). The rise of temperature seems chiefly to have this influence that some molecules (the number of which is indicated by the wellknown thermodynamic relations) *suddenly* break up into simpler ones or the reverse), when the strong chemical bond is broken for *these* molecules in consequence of the too great intensity of the internal motions. Then in the "dissociating" substance there are simply *two kinds* of molecules, e.g. for N_2O_4 the molecules N_2O_4 and NO_2 , but — *as long as they exist individually* — both seem to be pretty insensible to changes of volume by temperature or pressure.

And finally — when the so-called *quasi-association* is considered as a phenomenon inherent in the nature of things: I mean in this sense that *temporary molecule aggregations* are naturally formed

without any special cause, in consequence of collisions, and of the temporarily acting strengthened attractive forces, or by other accidental circumstances — so that this state of quasi-association¹⁾ for every substance is quite determined by the value of the (reduced) temperature and of the volume — we are naturally led to combine all the influences mentioned into one equation $b = f(v, T)$, of which at present we only know the general form, without being able to define it more closely. It seems to me that the final decision — as regards the derivation of the equation in question — will be given again by the radiation theory and the theory of quanta.

2. Before giving the new relation between the critical quantities, found by me some time ago, we may briefly state the results of the foregoing paper, as far as the relations existing between the critical quantities are concerned.

When $b = f(v)$ is assumed, and $\left(\frac{\partial b}{\partial v}\right)_k$ and $\left(\frac{\partial^2 b}{\partial v^2}\right)_k$ is indicated by b'_k and b''_k , putting $v_k : b_k = r$, it follows from the equation of state

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

in the first place, by putting $\left(\frac{dp}{dv}\right)_T$ and $\left(\frac{d^2p}{dv^2}\right)_T = 0$ (loc. cit. p. 45 et seq.):

$$\frac{r-1}{r} = \frac{2}{3} \frac{1-b'_k}{1^{-1}/_3 b''_k}, \dots \dots \dots (1)$$

when $\beta''_k = v_k b''_k : (1-b'_k)$.

Further

$$\left. \begin{aligned} RT_k &= \frac{8}{27} \lambda_1 \frac{a}{b_k}, \text{ in which } \lambda_1 = \frac{27}{8} \frac{(r-1)^2}{r^3} \frac{2}{1-b'_k} \\ p_k &= \frac{1}{27} \lambda_2 \frac{a}{b_k^2}, \quad \text{,,} \quad \lambda_2 = \frac{27}{r^3} \left[\frac{r-1}{r} \frac{2}{1-b'_k} - 1 \right] \end{aligned} \right\} \dots \dots (2)$$

In this λ_1 and λ_2 are never far from 1; for substances that deviate most from those which would correspond to the ideal VAN DER WAALS's equation of state — the latter will henceforth be called "ideal substances" for shortness — λ_1 and λ_2 are both = 0,98.

For the so-called critical coefficient $s = RT_k : p_k v_k$ is found:

$$s = \frac{\lambda_1}{\lambda_2} \frac{8}{r}, \dots \dots \dots (3)$$

in which $\lambda_1 : \lambda_2$ may always be put = 1.

¹⁾ Which according to this view has therefore *nothing* to do with *real* association, as for NO₂ and H₂O, which is of entirely *chemical* nature.

If $p : p_k = \varepsilon$, $T : T_k = m$, $v : v_k = n$, $b : v_k = \beta$ may be put, the reduced equation of state, in consequence of the mentioned relations, becomes :

$$\left(\varepsilon + \frac{27 : \lambda_2 r^2}{n^2} \right) (n - \beta) = sm \dots \dots \dots (b)$$

Another set of equations is found by the introduction of the critical pressure coefficient $f = \left(\frac{T dp}{p dT} \right)_k$. But in this the dependence on the temperature of the quantity b must be taken into account. We easily find (see p. 56—57 loc. cit.):

$$f = \frac{RT_k}{p_k(v_k - b_k)} \left(1 + \frac{v_k}{v_k - b_k} \beta'_t \right),$$

when β'_t represents $\frac{T_k}{v_k} \left(\frac{\partial b}{\partial T} \right)_k$. Hence this becomes :

$$f = s \frac{r}{r-1} \left(1 + \frac{r}{r-1} \beta'_t \right).$$

If now the temperature-correction $\frac{r}{r-1} \beta'_t$ is represented by φ , and

if we bear in mind that $s \frac{r}{r-1}$ would be the value of f , when b (or a) were *no* function of the temperature, which value we shall henceforth denote by f' , we have the relation :

$$f' = s \frac{r}{r-1} = \frac{\lambda_1}{\lambda_2} \frac{8}{r-1}, \dots \dots \dots (4)$$

in which

$$f' = \frac{f}{1 + \varphi} \dots \dots \dots (5)$$

In this f is therefore the quantity $\left(\frac{d\varepsilon}{dm} \right)_k$ determinable *experimentally*, which, however, will not appear as such in the different relations. In them f' occurs systematically, which is connected with f by the relation (5). Fortunately, however, φ is always very small, so that in a first approximation f may be substituted for f' . But for the sake of accuracy we have everywhere in what follows not identified f' with f .

When $p_k + a/v_k^2$ is substituted for $RT_k : (v_k - b_k)$

$$f' - 1 = \frac{1}{\lambda_2} \frac{27}{r^2} = \frac{\lambda_2}{\lambda_1^2} \frac{27}{64} s^2, \dots \dots \dots (6)$$

follows from $f' = RT_k : p_k(v_k - b_k)$, so that we have also the relations:

$$r = \frac{3}{\sqrt{\lambda_2 \frac{f'-1}{3}}} ; \quad s = \frac{8}{3} \sqrt{\frac{\lambda_1^2 f'-1}{\lambda_2 \frac{f'-1}{3}}} \quad (6a)$$

while now the reduced equation of state may be written:

$$\left(\varepsilon + \frac{f'-1}{n^2} \right) (n-\beta) = sm, \quad \dots \quad (c)$$

in which f'' will always be *slightly* smaller than f .

3. If we assume for an "ordinary substance" (which is therefore farthest from the above mentioned "ideal substance") $s=3,77^1$, hence $1/s=0,2653$, then the value 2,12 corresponds to this for r , with $\lambda_1 \cdot \lambda_2 = 1$ according to (3).

Then the value 7,136 is found for f' from (4) with r ($r-1$)=1,893. Since f will have to be somewhat greater than f'' , as in (5) φ is positive at any rate, but as for f' experimentally a value is found which for the said substances if not very near 7,14, yet lies only little higher, we see confirmed here what I observed already above (see also loc. cit. p. 57), that φ will be exceedingly small at the critical temperature, and that therefore f'' and f will differ very little.

Further follows from $f'' - 1 = 27 : \lambda_2 r^2$, with $27 : r^2 = 27 \cdot 4,494 = 6,008$, for λ_2 the value $0,979 = \underline{0,98}$.

And from $f'' = (\lambda_1 : \lambda_2) \times (8 (r-1))$ the value $0,999 = 1$ for $\lambda_1 \lambda_2$ is then properly found back with $8 (r-1) = 7,143$, after which 0,98 is also found for λ_1 .

The quantities λ_1 and λ_2 will vary between 0,98 and 1, according as one descends from "ordinary substances" to "ideal substances" through the whole region of substances. In this r will at the same time vary from 2,12 to 3, s from 3,77 to 2,67, and f from 7 to 4.

We further find for the relation for λ_1 indicated in (2):

$$1 - b'_k = \underline{0,9085} \quad ; \quad b'_k = \underline{0,0915}.$$

The value of β''_k may be calculated from (1). We then find:

$$\beta''_k = v_k b''_k : (1 - b'_k) = \underline{-0,4398} \quad ; \quad v_k b''_k = \underline{-0,3996}.$$

In the above we only *apparently* started from one fundamental quantity, viz. s , from which we have calculated $r = 2,12$. For we then made use of the circumstance that $\lambda_1 : \lambda_2 = 1$ may be put.

Strictly speaking we ought to have assumed *two* quantities, viz.

¹⁾ Mean of the values 3,766 for *n*-Pentane, 3,735 for *i*-Pentane, 3,796 for Fluorbenzene.

s and r , from which all the other quantities can then be calculated. For r we could then have *assumed* 2,12, and we had then *found* $\lambda_1 : \lambda_2 = 1$. But it is better to start from two quantities, which are *experimentally* determinable. And for the present s and f' seem the most suitable, even though s depends on the accurate determination of the *critical density* (which is often very difficult, and generally takes place through the strictly speaking unpermissible prolongation of the so called "straight diameter" -- unpermissible, because this straight diameter exhibits a perceptible curvature *close* to the critical point), and though the determination of f' (supposing we may put $f' = f$) is from the nature of the thing always connected with not very accurate calculations of pressure and temperature *differences* close to the critical point.

We might e.g. have assumed $s = 3,77$ and $f' = 7$, and we had then also found $\lambda_1 = \lambda_2 = 0,98$. And the equality of λ_1 and λ_2 would also have become clear for other substances, as Oxygen, Argon etc., where another set of values for s and f' had been started from.]

We shall, however, immediately see that in consequence of the new relation found by me--instead of f' and s another quantity can be introduced, which in contrast with the two mentioned ones is experimentally pretty sharply definable. We mean the direction of the *straight diameter*, which can be determined very accurately from observations even far below the critical temperature, and is at any rate not affected by any uncertainty in the observations *close* to the critical temperature. T_k and v_k will, indeed, of course be of influence in the determination of the "reduced" coefficient of direction.

If, as said, we take, however, for the present f' and s , we find easily from the above relations :

$$r = \frac{f'}{f' - s} \quad ; \quad r - 1 = \frac{s}{f' - s} \quad (\alpha)$$

Further from $f' - 1 = 27 : \lambda_2 r^2$ and $f' = (\lambda_1 : \lambda_2) \times (8 : (r - 1)) :$

$$\lambda_1 = \frac{27}{8} \frac{s}{f' - 1} \left(1 - \frac{s}{f'}\right) \quad ; \quad \lambda_2 = \frac{27}{f' - 1} \left(1 - \frac{s}{f'}\right)^2, \quad . . . (\beta)$$

through which :

$$\frac{\lambda_1}{\lambda_2} = \frac{s}{8(1 - s/f')} \quad (\gamma)$$

Finally we shall find :

$$1 - b'_k = \frac{2s(f' - 1)}{f'^2} \quad ; \quad -\beta''_k = -\frac{v_k b''_k}{1 - b'_k} = \frac{f' - 4}{f'} \quad . (\delta)$$

In this particularly the last relation, viz. for β''_k , is remarkably

simple, the more so as there occurs only one quantity, viz. f' , in it. For $f' = f = 4$ we have $\beta'_k = 0$, as we should have.

4. If we may really put $\lambda_1 : \lambda_2 = 1$, s is perfectly determined by f' through the relation (7), and only one quantity either s or f' suffices. Then we have only to put:

$$s = \frac{8f'}{8+f'} \quad \text{or} \quad f' = \frac{8s}{8-s}$$

everywhere in the above. Further in (3) rs simply becomes $= 8$ and in (4) f' will become $= 8 : (r-1)$.

Hence if we express everything in f' , we have:

$$\left. \begin{aligned} s = \frac{8f'}{8+f'} \quad ; \quad r = \frac{8+f'}{f'} = 1 + \frac{8}{f'} \quad ; \quad \lambda = \frac{27f'^2}{(f'-1)(8+f')^2} \\ 1 - b'_k = \frac{16(f'-1)}{f'(8+f')} \quad ; \quad -\beta'_k = \frac{f'-4}{f'} \end{aligned} \right\} \quad (7)$$

by the side of which we mention a few more earlier relations in the new form:

$$\left. \begin{aligned} rs = 8 \quad ; \quad f'(r-1) = 8 \quad ; \quad \lambda(f'-1) = \frac{27}{r^2} = \frac{27}{64} s^2 \\ r = 3 : \sqrt{\lambda(f'-1)} : 3 \quad ; \quad s = \frac{8}{3} \sqrt{\lambda(f'-1)} : 3 \end{aligned} \right\} \quad (8)$$

when $\lambda_1 = \lambda_2$ is represented by λ . We once more point out, that all the foregoing relations hold quite generally and perfectly accurately, but that the relations (7) and (8) will be dependent on the assumption $\lambda_1 : \lambda_2 = 1$. But this latter relation may be considered as perfectly accurate.

Now

$$RT_k = \frac{8}{27} \lambda \frac{a}{b_k} \quad ; \quad p_k = \frac{1}{27} \lambda \frac{a}{b_k^2}$$

is simply found for RT_k and p_k , so that we can calculate the quantities a and b_k very accurately from the observed critical pressure and temperature.

As for the quantity λ , it is $= 49 : 50 = 0,98$ for $f' = 7$; for $f' = 6$ we find $243 : 245 = 0,992$; for $f' = 5$ we have $\lambda = 675 : 676 = 0,9985$, and for $f' = 4$ the value 1 is found. So whereas $\lambda_1 : \lambda_2$ is pretty accurately $= 1$, $\lambda = \lambda_1 = \lambda_2$ will in the utmost case *only* deviate 2% from unity, and will approach more and more to 1 for substances with lower values for f' .

Let us now proceed to give the new relation and at the same time introduce the reduced coefficient of direction of the straight diameter γ .

5. *A new relation.*

I found, namely, that remarkably enough, there always exists a simple relation between the quantities $r = v_k : b_k$ and $z = b_k : v_0$. Not the *approximate* equality of s and $s' = v_k : v_0$, brought forward by VAN DER WAALS, but another *accurate* relation. For though s differs little from s' , yet the difference can amount to $1/8$ of the value, whereas the relation found by me seems perfectly accurate; the value of $s : s'$ can be calculated from it for every value of the chosen independent parameter.

We know that according to the property of the "straight diameter"

$$\frac{\frac{1}{2}(d_1 + d_2) - 1}{1 - m} = \gamma,$$

when d_1 and d_2 represent the reduced densities of liquid and vapour. When d_2 may be neglected with respect to d_1 , we have simply:

$$\frac{1}{2} d_1 = 1 + \gamma(1 - m),$$

which for $m = 0$ would pass into $\frac{1}{2} d_0 = 1 + \gamma$ or

$$d_0 = \frac{v_k}{v_0} = 2(1 + \gamma).$$

Here v_0 is therefore the fictitious *extrapolated* liquid volume at the absolute zero-point; this volume can of course not be realized for liquids, but in this ideal limiting case we may write b_0 for it — by b_0 we must, therefore, understand the same thing as is understood by v_0 , i.e. the smallest volume that a number of molecules lying closely together, so that they are all in contact with each other, can occupy.

So if in future we represent the relation $v_k : v_0$ by s' , and the relation $b_k : b_0$ by z , we have:

$$\frac{v_k}{b_0} = s' = 2(1 + \gamma); \quad \frac{b_k}{b_0} = z = \frac{s'}{r} = \frac{2(1 + \gamma)}{r}, \quad \dots \quad (9)$$

because $r = v_k : b_k$. So far these equations do not contain anything new; the last may serve to calculate z , when γ and r are known, in which r may be calculated from one of the equations (7), viz. $r = 1 + (8 : f')$. Thus $z = 1,8$ e.g. for an ordinary substance ($\gamma = 0,9$, $r = 2,12$); $z = 1,5$ for argon ($\gamma = 0,75$, $r = 2,33$); $z = 1$ for an ideal substance ($\gamma = 0,5$, $r = 3$).

But now I found that always:

$$z = \frac{2}{r-1} \dots \dots \dots (10)$$

for the most different substances. In this form the relation was first discovered by me. Thus among others:

For an ordinary substance ($f' = 7,2$)	$1,8 = \frac{2}{1,11} = 1,8$
„ Argon ($f' = 6$)	$1,5 = \frac{2}{1,33} = 1,5$
„ ideal substance ($f' = 4$)	$1 = \frac{2}{2} = 1$

in which the value of z in the first member was calculated from (9), i. e. from $z = 2(1 + \gamma) : r$.

The relation (10) seems, therefore, to hold very accurately. It comes to this that $r - 1 = 2 : z$, or

$$\frac{v_k - b_k}{b_k} = \frac{2 b_0}{b_k},$$

hence

$$\underline{v_k - b_k = 2 b_0} \dots \dots \dots (11)$$

If, namely, only for ideal substances we find $v_k - b_k = 2 b_k$, so that then v_k becomes $3 b_k$ — now this property appears to continue to hold for *all* substances, if only in the second member $2 b_0$ is substituted for $2 b_k$ (in which b_0 is therefore always the volume v_0 at $T = 0$ extrapolated from the equation of the straight diameter). As therefore

$$\underline{\frac{v_k}{b_0} - \frac{b_k}{b_0} = 2} \text{ or } \underline{s' - z = 2}, \dots \dots \dots (11a)$$

and as $v_k : b_0 = 2(1 + \gamma)$ according to (9), we also have simply:

$$\underline{z = \frac{b_k}{b_0} = 2 \gamma} \dots \dots \dots (12)$$

And this is what the new-found relation really comes to. In this way we have for

Ordinary substance	$\gamma = 0,9$	$z = 1,8$
Argon	$\gamma = 0,75$	$z = 1,5$
Ideal substance	$\gamma = 0,5$	$z = 1$

For an ideal substance we take $\gamma = 0,5$, because there just as for the other substances the coefficient of direction has been taken of the straight line which connects the critical point with the point d_0 at $m = 0$. The always slightly deviating direction of the locus $\frac{1}{2}(d_1 + d_2) = f(m)$ close to the critical point would be $= 0,4$. (Compare my earlier papers of 22 Nov. 1911, p. 438 et seq., of 24 Jan. 1912, p. 563 et seq. and 574, and of 25 April 1912, p. 1091 1096). That the so-called "straight diameter" really exhibits a slight curvature at the last moment in the immediate neighbourhood of the critical

point, has been found among others by CARDOSO for different substances.

From the above a remarkable relation can still be derived, namely, $s' - 2$ being $= z$ according to (11a), and z being $\frac{2}{r-1}$ according to (10):

$$s' - 2 = \frac{2}{r-1},$$

or as $r-1$ is always $= s: (f' - s)$ according to (a):

$$s' - 2 = 2 \frac{f' - s}{s},$$

from which immediately follows:

$$\underline{2f' = ss'} \dots \dots \dots (13)$$

Thus e.g.

Ordinary substance	$s = 3,77$	$s' = 3,8$	$f' = 7,16$
Argon	3,424	3,5	5,99
Ideal substance	2,667	3	4

Here attention must once more be drawn to the difference between $s = RT_k: p_k v_k$ and $s' = v_k: v_0$, which difference is, indeed, small, but never negligible. Thus for an ideal substance $s': s = 9/8$. The empirical equalisation of s' and s would only lead to *approximate* relations (v. D. W.), whereas our above empirical relations are perfectly exact, and seem to hold accurately for all substances.

6. The found relation between z and r (in (10)), and in connection with (9) therefore also between r and γ — which relation will have to be *theoretically* justified by the course of the function $b = f(v)$, through which $b_k: b_0$ becomes $= 2\gamma$ according to (12), which will be discussed presently — now enables us in connection with the assumption $\lambda_1: \lambda_2 = 1$, to express *all* the quantities relating to the equation of state in the one independent parameter γ .

In the first place we choose γ , because this quantity according to (12) is in the closest relation with the course of the function $b = f(v)$, on which after all everything is founded: all the difference between the great diversity of the substances. But in the second place because this quantity γ , as said, can be easily experimentally determined, as for this purpose only a number of liquid- and vapour densities must be determined not up to the critical temperature, but near to it.

From (9) and (10) follows with regard to r :

$$z = \frac{2(1+\gamma)}{r} = \frac{2}{r-1},$$

hence

$$r = \frac{1+\gamma}{\gamma} \dots \dots \dots (14)$$

Then from (3), viz. $rs = 8 \times (\lambda_1 : \lambda_2)$, when $\lambda_1 : \lambda_2 = 1$ is put,

$$s = \frac{8\gamma}{1+\gamma} \dots \dots \dots (15)$$

follows for s , whereas from $s' = 2(1+\gamma)$, (see (9)), follows:

$$\frac{s'}{s} = \frac{(1+\gamma)^2}{4\gamma} \dots \dots \dots (16)$$

From $f' = 8s : (8-s)$ (see a little above (7)), or also from $f' = \frac{8}{r-1}$ according to (4) we derive:

$$f' = 8\gamma, \dots \dots \dots (17)$$

an exceedingly simple relation, which states that the critical coefficient of pressure f' will always be equal to eight times the reduced coefficient of direction of the straight diameter.

From (7) follows for γ :

$$\lambda = \frac{27\gamma^2}{(1+\gamma)^2(8\gamma-1)} \dots \dots \dots (18)$$

Further according to (7) we have:

$$1-b'_k = \frac{8\gamma-1}{4\gamma(1+\gamma)}; \quad b'_k = \frac{(2\gamma-1)^2}{4\gamma(1+\gamma)}; \quad \frac{b'_k}{1-b'_k} = \frac{(2\gamma-1)^2}{8\gamma-1} \dots (19)$$

Then also according to (7):

$$-\beta'_{k'} = -\frac{v_k b''_k}{1-b'_k} = \frac{f'-4}{f'} = \frac{2\gamma-1}{2\gamma} \dots \dots (20)$$

Thus we arrive, substituting $b_k : b_0$ for 2γ according to (12), at the exceedingly simple relations at the critical point:

$$b'_k = \frac{(b_k - b_0)^2}{b_k v_k}; \quad -\beta'_{k'} = \frac{b_k - b_0}{b_k} \dots \dots \dots (21)$$

From this we can already get an insight into the probable values of b' and β'' also outside the critical point, and try to derive the relation $b = f(v)$ by integration. But this will be discussed later.

If we now finally summarize what has been found, in a table in which some principal types of known substances have been inserted, we get the following instructive summary, from which it may be seen how the whole behaviour of the substance can be deduced from one fundamental quantity — here the quantity γ (also $= \frac{1}{2}(b_k : b_0)$), the reduced coefficient of direction of the straight diameter according to $\frac{1}{2}(d_1 + d_2) - 1 = \gamma(1-m)$. We may further avail ourselves of the following table for the prediction of still un-

¹⁾ In which f' is properly speaking $= f : (1 + \varphi)$, see (5). But f' always differs exceedingly little from f .

known values (for helium and hydrogen e.g.) or for the *correction* of already determined values (among others for oxygen).

	γ	$s = \frac{b_k}{b_0}$	$r = \frac{v_k}{b_k}$	$s' = \frac{v_k}{v_0}$	s	$s' : s$	f'	λ	b'_k	$-\beta'_k$
Limiting substance ¹⁾	1	2	2	4	4	1	8	0.964	0.125	0.55
Ordinary substances ²⁾	0.9	1.8	2.11	3.8	3.79	1.003	7.2	0.977	0.0936	0.444
oxygen } Argon }	0.8	1.6	2.25	3.6	3.55	1.0125	6.4	0.988	0.0625	0.375
	0.75	1.5	2.33	3.5	3.43	1.02	6	0.992	0.0476	0.333
Hydrogen } Helium }	0.6	1.2	2.67	3.2	3	1.067	4.8	0.999	0.0104	0.167
	Ideal substance	0.5	1	3	3	2.67	1.125	4	1	0

Now for H_2 has been found $s = \pm 2,9$, $f = 4,83$; so this agrees very well with our type, where $\gamma = 0,6$ ($s = 3$, $f' = 4,8$). Accordingly we may expect for H_2 a straight diameter, the reduced coefficient of direction of which will amount to 0,6.

For helium has been found $s = 3,13$, $f > 4,46$; this too may be correct. If s is really 3,13, f' would even be greater than 5. But if f' is no more than 4,5, then γ would be = 0,56, and $s = 2,9$, just as for H_2 .

And, at last, for O_2 has been found $s = 3,346$, $f = 5,76$, $\gamma = 0,813$, where the values of s and f are in good harmony, but γ deviates greatly. For with $f = 5,76$ would correspond $\gamma = 0,72$, $s = 3,349$, so that s as has been said, agrees beautifully, but γ ought to be considerably lower than 0,813. But here the fact may also have influence that liquid oxygen is an *associated* liquid, and that hence (just as for ethyl and methylalcohol, acetic acid, etc.) γ is *higher* than the normal value.

7. We will not drop this subject before having set forth a few points. First: the circumstance, to which putting $\lambda_1 : \lambda_2 = 1$ really comes, is this. According to (γ) $\lambda_1 : \lambda_2 = s : 8(1 - s/f')$ and so when $\lambda_1 = \lambda_2$ is assumed, this comes to this that $s = 8f' : (8 + f')$ (see above (7)). This is experimentally satisfied. But further $f' = 8\gamma$ — also in consequence of the new relation (12) — and according to (21) $b'_k = (b_k - b_0)^2 : b_k v_k$. The latter is in connection with the form

¹⁾ Substance with high molecular weight.

²⁾ Mean of *n*-pentane, *i*-pentane, fluorbenzene, etc.

of the function $b = f(v)$, and so the particular form of this last function is after all the deeper cause that both $\lambda_1 = \lambda_2$, and the new relations found by me, viz. $v_k - b_k = 2b_0$ and $b_k : b_0 = 2\gamma$ are satisfied.

I further draw attention to the fact that the above relations only remain valid as long as the law of equipartition continues to hold at very low temperatures. I have convinced myself for argon that the departures from this law even at the lowest temperatures, at which vapour-pressure determinations etc. have still been made below the critical temperature — among others at 90° K. — are still so slight that they remain entirely below the errors of observation. But this will be treated more fully in a following communication. Whether this is the case at the critical temperatures of hydrogen and helium, I have not yet examined. It is, however, very well possible that for such exceedingly low absolute temperatures the deviations are large enough to give rise to more or less considerable deviations in the formulae. This can particularly affect the quantity γ , as the straight diameter extends to still lower temperatures than the critical temperatures.

Finally a few remarks on the way in which b depends on the temperature. It has appeared to me that this variability is exceedingly slight at higher temperatures, so that even at the critical temperature of ordinary substances $\frac{\partial b}{\partial T}$ is still negligible (See § 1 and 2). This is in agreement with what I found before for H_2 ¹⁾. For 0° , 100° , and 200° C. I found, namely, b_γ constant $= 917 \times 10^{-6}$ (p. 576, 580 and 582 loc. cit.). But b_0 varied greatly. That b_0 varied and even apparently *increased* according to the relation $b_\gamma - b_0 = \sqrt{\gamma T}$ was entirely owing to the form of the chosen function $b = f(v)$, viz. the wellknown "equation of state of the molecule" of VAN DER WAALS.

It has, however, become clear to me that this equation does not hold, and is in contradiction to the above given accurate values b'_k and β'_k . The fact is this that b *decreases* at *all* temperatures, but the more as the temperature is lower. Finally b_γ will have become $= b_0$ at the absolute zero; hence no variation of b with the volume will then be possible any more. For at a given temperature b moves between b_γ (for $v = \infty$) and b_0 (for $v = v_0$). Now b_γ is a temperature function, and it moves from b_∞ (for T large) to b_0 (for $T = 0$). Hence in a b, v -diagram at high temperatures the curve $b = f(v)$ will have a pretty steep inclination from $b_\gamma =$ about $1,9 b_0$ (for ordinary substances)

¹⁾ These Proc. of 24 April 1903, p. 573—589.

to b_0 . But at low temperatures this curve will approach the *straight* line $b = b_0$ more and more, moving from b_0 to b_0 .

Now as has been said, the decrease of b_g with T is so slow at first that $b_g = b_\infty$ at T very great is not very different from b_g at T_k , when namely T_k is comparatively high, as for all "ordinary" substances. Only at lower temperatures b_g decreases rapidly to b_0 .

In consequence of this $\frac{\partial b}{\partial T}$ will, therefore, be comparatively very small in the neighbourhood of T_k , but $\frac{\partial^2 b}{\partial T^2}$ will assume a much greater value.

So this accounts for the fact that for substances with *low* critical temperatures, as O_2 , Argon, H_2 and Helium the ratio $b_k : b_0$ becomes smaller and smaller (see the table), which will cause the type to *approach more and more* to that of the so-called ideal substance, where VAN DER WAAALS' ideal equation of state with constant b will hold. For once more: at lower temperatures b_g approaches b_0 more and more, and the distance between b_g and b_0 disappears.

But that this is not the *only* cause of the change of type, so that e.g. Xenon with a comparatively high critical temperature ($+16^\circ,6\text{C.}$) is identical in its behaviour with O_2 , where $T_k = -119^\circ\text{C.}$ — this is perhaps owing to this that a second circumstance can be of influence on the course of b as function of v , namely that the relation $\frac{v_0}{b_0}$, which will probably depend on the structure of the molecule (compound or simple as for argon, helium etc.), need not always be $= 1$. This too will be discussed later.

Both the varying value of b_g with decrease of temperature, and the variable value of $v_0 : b_0$ according to the nature of the different substances: these are the principal causes of the preservation of the individuality of the great majority of substances also in their *reduced* equation of state, so that these substances may be divided into different classes, ranging from the class of the "limiting substance" with high molecular weight, and of the ordinary substances, to that of the "ideal" substance with extremely low critical temperature, for which would hold $f = 4$, $r = 3$ and $s = \frac{5}{3}$. But even helium (see the table) is still a long way from this.

In a following paper we shall treat the form of the function $b = f(v)$, and test the found expressions by the values of b which I have calculated for Argon.

I will communicate already here, that of the many expressions which satisfy the relations (21), i.e. which at T_k give the values of

b'_k for β''_k indicated there, only some types lead to simple results¹⁾, among others also (with some restriction, see later on) the exponential type proposed already before by KAMERLINGH ONNES :

$$b = b_g - (b_g - b_0)e^{-\alpha(v-v_0)}$$

Already in 1901 (Archives Teyler (2) T. VII, Troisième partie) I tested (see p. 14 et seq.) the values of b for H_2 and CO_2 , by this equation²⁾, and found a good agreement. But that I then found deviations with respect to the critical quantities is simply owing to this that I at the time did not take b_g variable with the temperature, and that therefore observations of H_2 at 0° C. can by no means give a final decision about the quantities at -241° C.

It is of course only of formal importance, when in the above relation and others at last b_g and v_0 are replaced by critical quantities, so that the relations (21) are satisfied. But this will be discussed in a subsequent paper.

Fontainivent sur Clarens, January 1914.

Physics. — “An apparatus for the determination of gas isotherms up to about 3000 Atm.” (Continuation.) VAN DER WAALS-fund researches N^o. 6. By Prof. PH. KOHNSTAMM and K. W. WALSTRA. (Communicated by Prof. J. D. VAN DER WAALS.)

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

B. *The volume measurement.* (Continuation).

CONVEYANCE OF THE GAS INTO THE MEASURING TUBE.

In the previous communication the question was answered how the volume is determined of a quantity of gas which is in the measuring tube, above mercury. Now we shall have to describe how we get the gas quantity that is to be measured, in this position. For this the most intricate part of the apparatus is required.

As is known AMAGAT's measuring tubes consisted of piezometers

¹⁾ Also v. d. WAALS' relation in the general form $\frac{b-b_0}{v-b} = f \left[1 - \left(\frac{b-b_0}{b_g-b_0} \right)^n \right]$ with b_0 constant gives perfectly impossible results, among others n varying between 8 and 30.

²⁾ It is easy to see that the relation used there, viz.

$$b = b_\infty \left(1 - \theta e^{-\beta \frac{v}{b_\infty}} \right)$$

by the application of suitable substitutions for θ and β is identical with the above relation.