Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

VIII, $x = 0.114$

T	Δ	ph.	endc.	ph.
29°.9	69.15	pl.p.	69.15	pl.p.
31 .2	71.20	2 and 3	74.10	,,
32 .9	73.65	2 and 3	80.05	,,
34 .6	76.65	2 and 3	85,90	,,
35 .9	78.60—78.65	2 and 3	90.50	?
37 .4	81.60—81.65	2 and 3	95.95	
38 .9	84.15—84.20	2 and 3	100.90	
39 .9	86.60 ·	plp.	104.40	
41 .0			108.20	
42 .0			111.10	
43 .0			114.10	
44 .0			117.10	
44 .7			119.20	
45 .4			122.75	
46 .2			124.15	

tube burst

Physics. — "*The variability of the quantity b in* VAN DER WAALS' *equation of state, also in connection with the critical quantities.*" I. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. At the end of my last paper on the solid state (These Proc., May, 1911) I announced on p. 100 the fuller discussion of the problem alluded to in §§ 35 and 36. I may now be allowed to discuss this problem more at length.

In the paragraphs mentioned, particularly in § 35, I have already set forth at length how we can arrive at a complete theory of the variability of the quantity b, if we only assume that the molecules are *associated* to larger molecule complexes to an amount varying with the temperature and the volume, in which we must suppose the volumes of the complex molecules *smaller* than the corresponding volumes of the simple molecules which form the complex.

I think I have demonstrated (loc. cit.) in a convincing way that the two causes of the variability of b, which were kept separate before, are solved in, and are comprised by the wider theory of association — which naturally also includes the third cause recently brought forward by VAN DER WAALS — I mean the so-called "quasi"-association.

For the diminution of the molecular volume b in consequence of

the increasing association, on diminution of the volume v e. g., can be considered to be a *real* diminution of that molecular volume, but also as an *apparent* diminution accompanying it. The quantity $\Delta b = - b_1 + v b_2$ introduced in our theory need namely not necessarily indicate exclusively the *real* change of the volume of a molecule, but can also include the *apparent* change, in so far as it is manifested in its effect on the *pressure* in consequence of the temporary aggre-gations of the molecules (see p. 96 and 97 loc. cit.) [1]).

The degree of variability of b is then further exclusively determined by the degree of dissociation β of the compound molecule-complexes. As this quantity being a function both of v and T, the quantity b, given by $b = (1 - \beta) b_1 + v \beta b_2$, i. e. by

$$b = v b_2 - (1 - \beta) \Delta b,$$

will depend besides on v, also on T, though the latter will be the case only to a very small degree, as we shall show presently.

It is this way of considering the problem, which I dimly conceived already some ten years ago, and which I have practically never quite abandoned, though I adopted other points of view for a time. Now after the completion of my theory of the solid state, I am more than ever convinced that my original point of view must be the right one. Already the *course* of the quantity β as function of v and T made me see the great probability of this point of view. The way, namely, in which β for v and $T = 0$ approaches 0 asymp-totically (so that only complex molecules are then present), and approaches 1 asymptotically for v and $T = \infty$ (all the molecules simple); while the critical point appeared to lie exactly at the beginning of the abrupt inflection from 1 to 0 — which pointed to an appre-ciable value there of $b' = \dfrac{db}{dv}$, and to a rather considerable value of

$- v b'' = v \dfrac{d^2 b}{dv^2}$ — all this convinced me more and more that the variability of b was *only* and *exclusively* to be attributed to the varying degree of association of the molecules, *together* with the variation of volume Δb (real or apparent) attending it.

Whereas in the paper of VAN DER WAALS presently to be mentioned (loc. cit. p. 1227 and 1228), only an *empirical* relation could be

---

[1]) Exactly in the same way as among others REINGANUM, when he comes to the conclusion that the influence of the temperature on the pressure which the mole-cules of a non-ideal gas exert on the wall, is manifested in a *fictitious* enlarging of the molecule: it seems "*as if*" the molecules are enlarged with rise of tempera-ture ; etc.

given for the variability of b, holding only in the neighbourhood of the critical point, viz. $\dfrac{b}{b_q} = 1 - a\left(\dfrac{b_q}{v}\right)^{4,34}$, now a *theoretical* formula can be derived for this variability, which just as my theory for the Solid State, has a purely *physical* foundation.

Already in my Solid State VII I derived (p. 98—100) from the general formula an approximate formula, viz. $\dfrac{b}{b_q} = 1 - \psi\left(\dfrac{b_q}{v-b}\right)^2$, which in my opinion is preferable to van der Waals' empiric formula, though of course our approximative formula is not accurate either. But in what follows we shall make use of the original quite accurate formula $b = f(v,T)$.

The same quantities β and Δb, which play so important a part in the transition of the liquid state to the solid state, and the reverse — so that we may safely say: *no solid state without these quantities* — must also necessarily play a part in the theory of the liquid (and of the solid) state considered in itself.

So this furnishes one cause, both for the deviations of the behaviour of liquids from the original ideal equation of van der Waals, and for the solid state appearing at lower·temperatures. And so in this way the *whole* behaviour of a substance, also the appearance of the *three* states of aggregation with their gradual transition at *critical* temperatures, can be brought under one point of view.

This solves at the same time the question repeatedly put by van der Waals in his last paper but one (These Proc., April 1911) on the critical quantities (see among other p. 1212 at the bottom; p. 1222 in the middle; p. 1228 at the bottom): "What is, after all, the cause of the variability of b".

As *principal causes* he seems still to accept the real diminution by compressibility (p. 1212 loc. cit), and the apparent diminution in consequence of the partial overlapping of the distance spheres (see p. 1225 and 1226 where the coefficient $a = \sqrt[3]{}/_8$ occurring in this case is mentioned). The so-called quasi-association would play only a negligible part (at least at the critical temperature) (see p. 1213 at the bottom).

In our theory, on the other hand, the association, with which the quasi-association is practically identical (see p. 93—94 of my last paper on the solid state), is the *only* factor — and it will appear from what follows that the critical quantities are also perfectly accurately determined by the *sole* assumption of *association*, with the *variation of volume* Δb accompanying it. We shall find that at the critical point the compound molecules are decomposed to an amount

$\beta = 0,95$ into simple molecules (so only $^1/_{20}$ part is still complex), while on assumption of an association to double or triple molecules in the neighbourhood of the critical point the value of Δb is found to be such that the limiting volume ($b_g = vb_2$ for $v = \infty$) has duly decreased to half its original size ($b_0 = b_1$, where $b_1 = {}^1/_2 vb_2$), when v has become $= b$.

To this is added the circumstance that the minimum molecular volume b_0 for $v = b$ proves to be the same for every temperature. For however high or low the temperature may be, β will always be $= 0$ in the expression (1) for β (see § 2) for $v = b$; hence $b_0 = b_1$, in which b_1 is the molecular volume of the complex molecules, on account of the above expressions for b and Δb. And reversely the value of b_0 will again be $= b_1$ for $T = 0$ for every volume, because also for $T = 0$ the degree of dissociation β will approach to 0. Hence there is not only one limiting volume for great volume and high temperature, but also only one limiting volume for small volume and low temperature; the latter about half the first.

The differences which continue to exist for different substances in the reduced equation of state, and which VAN DER WAALS p. 1212 pointed out, can now also easily be accounted for by a somewhat divergent value of β (and possibly also of Δb). For it is clear that the degree of dissociation of the complex molecules will not be the same for every substance. It will of course entirely depend on the constants of the equation of dissociation (1). And thus substances will also be found with abnormally greatly divergent values of β, the so-called *anomalous* substances.

Also the value of v can be different. It will namely also depend on the constants of the substance, *how many* molecules wil combine to a complex molecule at different temperatures and volumes. I have already pointed out in my last paper on the solid state (p. 98 at the bottom) that also v will be a function of v and T, and that on an average a greater number of molecules will associate at low temperature and small volume than at high temperature and great volume. But in our following considerations we shall for the present neglect *this* dependence, because we shall confine ourselves exclusively to the critical quantities. And at this volume and this temperature v will appear to be about from 2 to 3, i. e. the few molecules which are still associated then (about $^1/_{20}$) will be on an average associations of double or triple molecules. [At $T = \infty$ and $v = \infty$ the exceedingly few complex molecules, still present then, the number of which approaches to 0, will only be double ones of course].

In my last paper I came to the conclusion (p. 100) that v is about

3 at the critical point. But this was only an approximative calculation: a more accurate calculation makes us find a value of 2 à 3 for v.

But now we proceed to derive the critical quantities from the equation of state on the supposition of the variability of b exclusively in consequence of the dependence of the degree of dissociation β on the volume v; while RT has to be multiplied by the factor $1 + (v-1)\beta$, because in all there are $1-\beta$ complex molecules and $v\beta$ simple molecules, in which v will denote the number (for the present considered constant by us, see above) of simple molecules which are on an average associated to one complex molecule.

Also the quantity a will be assumed to be constant by us (see Solid State VII, p. 94 at the bottom, so that the contraction introduced by VAN DER WAALS in the value of a is not introduced in our derivations. The number of molecules associated to one complex molecule (on an average $2^1/_2$) is not great enough for it at the critical temperature, so that no reason whatever would exist for this contraction, (see also VAN DER WAALS, Quasiassociation. These Proc. XIII p. 119—121). So we consider the formula

$$a = n_1{}^2 a_1 + 2n_1 n_2 a_{12} + n_2{}^2 a_2$$

as valid, which passes into $a = a_1$ with $n_1 = 1 - \beta$, $n_2 = n\beta$, $a_{12} = \dfrac{a_1}{n}$, $a_2 = \dfrac{a}{n^2}$, in which (and this will henceforth be the case when the contrary is not asserted) always v-fold molecular quantities of the substance are considered.

The formulae following here were already derived by me in 1908, and published in the Arch. Teyler (2) **11**, Troisième Partie: "*Théorie de l'association* etc.", where (see p. 25—34) comparatively simple results were obtained. But these formulae only hold for the case $v = 2$, and we shall, therefore, give the derivation here once more for the perfectly general case that not 2, but v molecules are associated to a complex molecule, in which at the same time some simplications will be applied in the derivation.

2. The general formula for β was already derived for the case of v molecules in my Solid State VII p. 84 —86. We found there nl.:

$$\frac{\beta'}{(1-\beta)(1+(v-1)\beta)^{v-1}} = \frac{cT^{v+(v-1)} e^{-\frac{q_0}{RT}} e^{-\frac{v+a/v^2}{RT}\Delta b}}{(p+a/v^2)^{v-1}}.$$

If we substitute for $p + a/v^2$ the expression which follows for it from the equation of state

$$(p + a/v^2)(v-b) = (1 + (v-1)\beta)RT,$$

we get:

$$\frac{\beta'}{(1-\beta)(1+(v-1)\beta)^{\prime-1}} = \frac{cT^{\prime+(\prime-1)}e^{-\frac{q_0}{RT}}e^{-(1+(\prime-1)\beta)\frac{\Delta b}{v-b}}}{(1+(v-1)\beta)^{\prime-1}(RT)^{\prime-1}}(v-b)^{\prime-1},$$

or putting $v-1 = x$:

$$\frac{\beta^{x}+1}{(1-\beta)(1+x\beta)^{x}} = \frac{c}{R^{x}}\frac{T^{\prime}e^{-\frac{q_0}{RT}}e^{-(1+x\beta)\frac{\Delta b}{v-b}}}{(1+x\beta)^{x}}(v-b)^{x} \quad . \quad . \quad . \quad (1)$$

If now Δb is *positive*, i.e. if the complex molecules (real or apparent) occupy a smaller volume than the simple ones, the degree of dissociation β will get the value 0 for $v = b$, and the value 1 for $v = \infty$. In the same way the quantity β will approach to 0 at $T = 0$ for positive values of q_0 and γ, and at $T = \infty$ to 1.

In order to facilitate the following calculations, we put:

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

in consequence of which (1) passes into

$$\frac{\beta^{x}+1}{(1-\beta)(1+x\beta)^{x}} = \frac{\theta e^{-\varphi}}{\varphi^{x}}, \quad . \quad . \quad . \quad . \quad . \quad (1^{a})$$

in which θ represents the temperaturefunction $c\left(\frac{\Delta b}{R}\right)^{x} T^{\prime} e^{-\frac{q_0}{RT}}$.

The equation (1^{a}), combined with the equation of state

$$(p+a/v^2)(v-b) = (1+x\beta)RT, \quad . \quad . \quad . \quad . \quad (2)$$

will now represent the total amount of the considered substance, to which then $b = (1-\beta)b_1 + v\beta b_2$ can be added, i.e.

$$b = vb_2 - (1-\beta)\Delta b,$$

or vb_2 being the limiting volume for $v = \infty$ $(\beta = 1)$:

$$b = b_q - (1-\beta)\Delta b, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which β is given by (1^{a}), and Δb by $\Delta b = -b_1 + vb_2$.

Now in order to find the values of v, RT and p at the critical point, we shall only have to put $\left(\frac{dp}{dv}\right)_t$ and $\left(\frac{d^2p}{dv^2}\right)_t$ equal to 0.

From the equation (2) in the form

$$p = \frac{(1+x\beta)RT}{v-b} - \frac{a}{v^2} = \frac{\varphi RT}{\Delta b} - \frac{a}{v^2}$$

follows (for T constant):

$$\frac{dp}{dv} = \frac{2a}{v^3} + \frac{RT}{\Delta b}\frac{d\varphi}{dv}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

in which we must therefore calculate $\dfrac{d\varphi}{dv}$. From (α) in the form

$$(1+x\beta)\,\Delta b = \varphi\,(v-b)$$

follows :

$$x\Delta b\,\frac{d\beta}{dv} = \varphi\left(1 - \Delta b\,\frac{d\beta}{dv}\right) + (v-b)\,\frac{d\varphi}{dv},$$

because $\dfrac{db}{dv} = \Delta b\,\dfrac{d\beta}{dv}$ according to (3).

Hence :

$$(v-b)\,\frac{d\varphi}{dv} = -\,\varphi + (x+\varphi)\,\Delta b\,\frac{d\beta}{dv}\,. \qquad \ldots \quad (\gamma)$$

So we have to calculate $\dfrac{d\beta}{dv}$, and that from (1^a). This relation, differentiated logarithmically, yields .

$$\left(\frac{x+1}{\beta} + \frac{1}{1-\beta} - \frac{x^2}{1+x\beta}\right)\frac{d\beta}{dv} = -\frac{d\varphi}{dv} - \frac{x}{\varphi}\,\frac{d\varphi}{dv}\,,$$

or

$$\frac{x+1}{\beta\,(1-\beta)\,(1+x\beta)}\,\frac{d\beta}{dv} = -\frac{x+\varphi}{\varphi}\,\frac{d\varphi}{dv}$$

If in this we substitute the value (γ) found just now for $\dfrac{d\varphi}{dv}$, we get:

$$\frac{x+1}{\beta\,(1-\beta)\,(1+x\beta)}\,\frac{d\beta}{dv} = -\frac{x+\varphi}{\varphi}\,\frac{-\,\varphi + (x+\varphi)\,\Delta b\,\dfrac{d\beta}{dv}}{v-b}\,,$$

or

$$\frac{d\beta}{dv}\left[\frac{x+1}{\beta\,(1-\beta)\,(1+x\beta)} + \frac{(x+\varphi)^2}{\varphi}\,\frac{\Delta b}{v-b}\right] = \frac{x+\varphi}{v-b}\,,$$

or also

$$\frac{v-b}{1+x\beta}\,\frac{d\beta}{dv} = \frac{x+\varphi}{\dfrac{x+1}{\beta\,(1-\beta)} + \dfrac{(x+\varphi)^2}{\varphi}\,(1+x\beta)\,\dfrac{\Delta b}{v-b}}$$

i. e. taking (α) into account :

$$\frac{v-b}{1+x\beta}\,\frac{d\beta}{dv} = \frac{x+\varphi}{\dfrac{x+1}{\beta\,(1-\beta)} + (x+\varphi)^2}\,,$$

for which we may also write :

$$\frac{v-b}{1+x\beta}\frac{d\beta}{dv}=\frac{\dfrac{1}{x+1}\,\beta\,(1-\beta)\cdot(x+\varphi)}{1+\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2}.\quad\ldots\ldots\quad (d)$$

So we find finally, substituting (d) in (γ):

$$(v-b)\frac{d\varphi}{dv}=-\varphi+(1+x\beta)\frac{\Delta b}{v-b}\frac{\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^3}{1+\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2},$$

or as $(1+x\beta)\dfrac{\Delta b}{v-b}=\varphi$:

$$(v-b)\frac{d\varphi}{dv}=-\frac{\varphi}{1+\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2}\quad\ldots\ldots\quad (\varepsilon)$$

Now we get for $\dfrac{dp}{dv}$, by substitution of this value in (β):

$$\frac{dp}{dv}=\frac{2a}{v^3}-\frac{RT}{\Delta b\,(v-b)}\frac{\varphi}{1+\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2}\quad\ldots\quad (4)$$

As also $\dfrac{d^2p}{dv^2}$ must be $=0$, we have, when the equation

$$2a\frac{v-b}{v^3}=\frac{RT}{\Delta b}\frac{\varphi}{1+\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2}$$

is logarithmically differentiated :

$$\frac{1}{v-b}\left(1-\frac{db}{dv}\right)-\frac{3}{v}=\frac{1}{\varphi}\frac{d\varphi}{dv}-\frac{1}{1+y}\frac{dy}{dv},$$

when for shortness we put the expression $\dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2$ for a

moment $=y$. Hence, as $\dfrac{db}{dv}=\Delta b\dfrac{d\beta}{dv}$:

$$1-\frac{3(v-b)}{v}-\Delta b\frac{d\beta}{dv}=-\frac{1}{1+y}-\frac{1}{1-y}(v-b)\frac{dy}{dv},$$

because $(v-b)\dfrac{d\varphi}{dv}$ is equal to $-\dfrac{\varphi}{1+y}$ according to (ε). Hence we get.

$$3\frac{v-b}{v}=\frac{(2+y)-(1+y)\,\Delta b\,\dfrac{d\beta}{dv}+(v-b)\dfrac{dy}{dv}}{1+y},$$

or also

$$\frac{v-b}{v} = \frac{2}{3} \frac{(1+\frac{1}{2}y) - \frac{1}{2}(1+y)\,\Delta b\,\frac{d\beta}{dv} + \frac{1}{2}(v-b)\frac{dy}{dv}}{1+y} \quad . \quad . \quad (\varphi)$$

For $(1+y)\,\Delta b\,\dfrac{d\beta}{dv}$ we find according to (d), taking into account that

$(1 + x\beta)\,\dfrac{\Delta b}{v-b} = \varphi$:

$$(1+y)\,\Delta b\,\frac{d\beta}{dv} = \frac{1}{x+1}\,\beta(1-\beta)\,\varphi\,(x+\varphi).$$

The value of $\dfrac{dy}{dv}$ is found from

$$y = \frac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2,$$

from which follows:

$$(v-b)\frac{dy}{dv} = \frac{1}{x+1}\left[2\beta(1-\beta)\,(x+\varphi)\,(v-b)\frac{d\varphi}{dv} + (1-2\beta)(x+\varphi)^2\,(v-b)\frac{d\beta}{dv}\right].$$

With $(v-b)\dfrac{d\varphi}{dv} = -\dfrac{\varphi}{1+y}$ (see e)), and $(v-b)\dfrac{d\beta}{dv} = \dfrac{1}{x+1}\beta(1-\beta)(1+x\beta)$

$(x+\varphi) : 1+y)$ (see (d)) this becomes:

$$(v-b)\frac{dy}{dv} =$$

$$= \frac{1}{(x+1)(1+y)}\left[-2\beta(1-\beta)\varphi(x+\varphi) + \frac{1}{x+1}\beta(1-\beta)(1+x\beta)(1-2\beta)(x+\varphi)^3\right]\;\psi)$$

Hence

$$(v-b)\frac{dy}{dv} - (1+y)\,\Delta b\,\frac{d\beta}{dv} =$$

$$= \frac{1}{(x+1)(1+y)}\left[-2\beta(1-\beta)\,\varphi(x+\varphi) - (1+y)\,\beta(1-\beta)\,\varphi(x+\varphi) + \right.$$

$$\left. + \frac{1}{x+1}\,\beta(1-\beta)\,(1+x\beta)\,(1-2\beta)\,(x+\varphi)^3\right],$$

so that we find:

$$\frac{v-b}{v} = \frac{2}{3}\frac{1}{(1+y)^2}\left[(1+\tfrac{1}{2}y)\,(1+y) + \right.$$

$$+ \frac{1}{2(x+1)} \left\{ \begin{array}{l} -2\beta(1-\beta)\varphi(x+y) + \dfrac{1}{x+1}\beta(1-\beta)(1-2\beta+2x\beta-3x\beta^2)(x+\varphi)^3 \\[2mm] -(1+y)\beta(1-\beta)\varphi(x+\varphi) - \dfrac{x}{x+1}\beta^2(1-\beta)^2(x+\varphi)^3 \end{array} \right\} \Bigg] ,$$

as $(1+x\beta)(1-2\beta) = (1-2\beta+2x\beta-3x\beta^2) - x\beta(1-\beta)$.

Now we get further for the factor between [ ]:

$$1 + \frac{3}{2}\frac{1}{x+1}\beta(1-\beta)(x+\varphi)^3 +$$

$$+ \frac{1}{2(x+1)^2}\beta^2(1-\beta)^2(x+\varphi)^4 - \frac{1}{x+1}\beta(1-\beta)\varphi(x+\varphi) - \frac{1+y}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi) +$$

$$+ \frac{1}{2(x+1)^2}\beta(1-\beta)(1+2(x-1)\beta-3x\beta^2)(x+\varphi)^3 - \frac{x}{2(x+1)^2}\beta^2(1-\beta)^2(x+\varphi)^3 .$$

In this we have:

$$\frac{3}{2}\frac{1}{x+1}\beta(1-\beta)(x+\varphi)^3 = \frac{3x}{2(x+1)}\beta(1-\beta)(x+\varphi) + \frac{3}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi),$$

so that the factor mentioned becomes:

$$1 + \frac{3x}{2(x+1)}\beta(1-\beta)(x+\varphi) + \frac{1}{2(x+1)^2}\beta(1-\beta)(1+2(x-1)\beta-3x\beta^2)(x+\varphi)^3 + S,$$

in which the supplementary piece S is represented by

$$S = \frac{3}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi) - \frac{1}{x+1}\beta(1-\beta)\varphi(x+\varphi) + \frac{1}{2(x+1)^2}\beta^2(1-\beta)^2(x+\varphi)^4 -$$

$$- \frac{x}{2(x+1)^2}\beta^2(1-\beta)^2(x+\varphi)^3 - \frac{1+y}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi) .$$

The first two terms give $\dfrac{1}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi)$; the two following

ones $\dfrac{1}{2(x+1)^2}\beta^2(1-\beta)^2\varphi(x+\varphi)^3$; so that the first four terms can be represented by

$$\frac{1}{2(x+1)}\beta(1-\beta)\varphi(x+\varphi)\left[1 + \frac{1}{x+1}\beta(1-\beta)(x+\varphi)^2\right],$$

and this is evidently the fifth term apart from the sign. So the supplement S is $= 0$, and we finally get:

$$\frac{v-b}{v} = \frac{2}{3}\frac{1}{(1+y)^2}\left[1 + \frac{3}{2}\frac{x}{x+1}\beta(1-\beta)(x+\varphi) + \right.$$

$$\left. + \frac{1}{2(x+1)^2}\beta(1-\beta)(1+2(x-1)\beta-3x\beta^2)(x+\varphi)^3 \right].$$

If we henceforth put:

$$1 + y = 1 + \frac{1}{x+1}\,\beta(1-\beta)(x+\varphi)^2 = m$$

$$1 + \frac{3x}{2(x+1)}\,\beta(1-\beta)(x+\varphi) + \frac{1}{2(x+1)^2}\,\beta(1-\beta)(1+2(x-1)\beta-3x\beta^2)'x+\varphi)^2 = n \tag{5}$$

we find the simple expressions

$$\frac{v_k}{v_k-b_k} = \frac{3m^2}{2n} \quad ; \quad \frac{v_k}{b_k} = \frac{3m^2}{3m^2-2n} \cdot \quad \ldots \quad \ldots \tag{6}$$

For $x = 1$ ($v = 2$) the expressions for m and n pass into those which are to be found in the cited paper in the Arch. TEYLER (p. 29).

If $\beta = 0$ or 1 (one kind of molecules), m and n duly become $= 1$ and the old value 3 is found back for $\frac{v_k}{b_k}$.

Now the value of RT_k is easily found from (4) by putting $\frac{dp}{dv} = 0$. Then we get:

$$RT_k = \frac{2a}{v^3}\,\frac{\Delta b(v-b)}{\varphi}\,m,$$

or φ being $= (1+x\beta)\dfrac{\Delta b}{v-b}$:

$$RT_k = \frac{1}{1+x\beta}\,\frac{2a}{v^3}\,(v-b)^2\,m.$$

With $\dfrac{v-b}{v} = \dfrac{2n}{3m^2}$, $\dfrac{b}{v} = \dfrac{3m^2-2n}{3m^2}$ the last expression becomes:

$$RT_k = \frac{1}{1+x\beta} \cdot \frac{2a}{b} \cdot \frac{3m^2-2n}{3m^2} \cdot \frac{4n^2}{9m^4} \cdot m,$$

hence:

$$RT_k = \frac{1}{1+x\beta}\,\frac{8}{27}\,\frac{a}{b_k}\,\frac{n^2(3m^2-2n)}{m^5} \quad \ldots \quad , \quad . \tag{7}$$

If $\beta = 0$, this becomes ($m = 1, n = 1$) $RT_k = \dfrac{8}{27}\dfrac{a}{b_k}$. And if $\beta = 1$, we get e. g. for $x = 1$ ($v = 2$), $RT_k = \dfrac{1}{2} \cdot \dfrac{8}{27}\dfrac{a}{b_k}$. But as then the quantities a and b refer to *double*-molecular quantities, we have $a = 4a'$ and $b = 2b'$, hence $RT_k = \dfrac{8}{27}\dfrac{a'}{b'_k}$ as before, where a' and b' now refer to single molecular quantities.

Formula (7) occurs (for $x = 1$) in TEYLER on p. 31 (formula (16)).

At last the expression for p_k follows from the equation of state (2). The latter yields:

$$p_k = \cfrac{\cfrac{8}{27}\,\cfrac{a}{b}\,\cfrac{n^2\,(3m^2 - 2n)}{m^5}}{\cfrac{2n}{3m^2 - 2n}\,b} - \cfrac{a}{\left(\cfrac{3m^2}{3m^2 - 2n}\,b\right)^2},$$

as $v - b = \dfrac{2n}{3m^2 - 2n}\,b$, as immediately follows from (6). Hence

$$p_k = \frac{4}{27}\,\frac{a}{b^2}\,\frac{n\,(3m^2 - 2n)^2}{m^5} - \frac{1}{9}\,\frac{a}{b^2}\,\frac{(3m^2 - 2n)^2}{m^4},$$

i. e.

$$p_k = \frac{1}{27}\,\frac{a}{b_k^2}\,\frac{(3m^2 - 2n)^2(4n - 3m)}{m^5}, \quad \ldots \quad (8)$$

identical with what we found in Teyler, p. 32 (formula (17)).

Here too $p_k = \dfrac{1}{27}\,\dfrac{a}{b_k^2}$ is duly found both with $\beta = 0$ and with $\beta = 1$ ($m = n = 1$). Just as in the formulae for v_k and RT_k, b is then constant, and b_k is either $= b_1$ (if $\beta = 0$), or $= b_2$ (if $\beta = 1$).

Of the greatest importance is particularly the knowledge of the quantity $\mu = \dfrac{p_k v_k}{RT_k}$. For this we find now:

$$\mu = \cfrac{\cfrac{1}{27}\,\cfrac{a}{b_k^2}\,\cfrac{(3m^2 - 2n)^2(4n - 3m)}{m^5}\;\cfrac{3m^2}{3m^2 - 2n}\,b_k}{\cfrac{1}{1 + x\beta}\,\cfrac{8}{27}\,\cfrac{a}{b_k}\,\cfrac{n^2(3m^2 - 2n)}{m^5}},$$

or

$$\mu = (1 + x\beta)\frac{3}{8}\,\frac{m^2(4n - 3m)}{n^2} \quad \ldots \quad \ldots \quad (9)$$

For $\beta = 0$ this becomes $\mu = \dfrac{3}{8}$; for $\beta = 1$, and e.g. $x = 1$ ($v = 2$) we find $2 \times \dfrac{3}{8}$. But it must then again be borne in mind that then for the calculation of μ the critical volume of a *double* molecular quantity of substance has been taken for v_k. Hence if $\beta = 1$, so that we only have simple molecules, the value — if v_k refers to a single molecular quantity as usual — must still be divided by 2, and we get again $\dfrac{3}{8}$.

Formula (9) corresponds with (18) on p. 32 in Teyler.

3. Of just as great importance is also the knowledge of the quantity

$$f = \left(\frac{T}{p}\frac{dp}{dT}\right)_k.$$

From

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

follows :

$$\left(\frac{dp}{dT}\right)_v = \frac{(1+x\beta)R}{r-b} + \frac{xRT}{v-b}\left(\frac{d\beta}{dT}\right)_v + \frac{(1+x\beta)RT}{(v-b)^2}\Delta b \left(\frac{dp}{dT}\right)_v,$$

hence

$$T\left(\frac{dp}{dT}\right)_v = \left(p + \frac{a}{v^2}\right) + \frac{RT^2}{v-b}\left(\frac{dp}{dT}\right)_v\left[x + (1 + x\beta)\frac{\Delta b}{v-b}\right],$$

or also, in virtue of (a) :

$$T\left(\frac{dp}{dT}\right)_c = \left(p + \frac{a}{v^2}\right)\left[1 + \frac{1}{1+x\beta}T\left(\frac{d\beta}{dT}\right)_v(x+q)\right].$$

So we must calculate $\left(\dfrac{d\beta}{dT}\right)_v$. From (1^a) follows immediately by logarithmic differentiation (see for the first member also the calculation for $\left(\dfrac{d\beta}{dv}\right)_t$) :

$$\frac{x+1}{\beta(1-\beta)(1+x\beta)}\frac{d\beta}{dT} = \frac{\gamma}{T} + \frac{q_0}{RT^2} - \frac{d\varphi}{dT} - \frac{x}{\varphi}\frac{d\varphi}{dT}$$

$$= \frac{q_0+\gamma RT}{RT^2} - \frac{x+\varphi}{\varphi}\frac{d\varphi}{dT}.$$

Now from $\varphi = (1 + x\beta)\dfrac{\Delta b}{v-b}$ follows :

$$\frac{1}{\varphi}\frac{d\varphi}{dT} = \frac{x}{1+x\beta}\frac{d\beta}{dT} + \frac{1}{v-b}\Delta b\frac{d\beta}{dT} = \frac{1}{1+x\beta}\frac{d\beta}{dT}\left(x + (1 + x\beta)\frac{\Delta b}{v-b}\right),$$

hence also

$$\frac{1}{\varphi}\frac{d\varphi}{dT} = \frac{x+\varphi}{1+x\beta}\frac{d\beta}{dT}.$$

So we get, as $q_0 + \gamma RT = q$:

$$\frac{x+1}{\beta(1-\beta)(1+x\beta)}\frac{d\beta}{dT} = \frac{q}{RT^2} - \frac{(x+\varphi)^2}{1+x\beta}\frac{d\beta}{dT},$$

so

$$\frac{d\beta}{dT} = \frac{\dfrac{q}{RT^2}}{\dfrac{x+1}{\beta(1-\beta)(1+x\beta)} + \dfrac{(x+\varphi)^2}{1+x\beta}} = \frac{\dfrac{1}{x+1}\beta(1-\beta)(1+x\beta)\dfrac{q}{RT^2}}{1 + \dfrac{1}{x+1}\beta(1-\beta)(x+\varphi)^2}$$

For f we may now write:

$$f = \left(1 + \frac{a}{pv^2}\right)\left[1 + \frac{q}{RT}\frac{\frac{1}{x+1}\beta(1-\beta)(x+\varphi)}{1 + \frac{1}{x+1}\beta(1-\beta)(x+\varphi)^2}\right] \quad . \quad (10)$$

We observe that the factor of $\frac{q}{RT}$ according to (d) is also

$$= \frac{v-b}{1+x\beta}\frac{d\beta}{dv}.$$

Formula (10) agrees with (28) on p. 42 in TEYLER ($x=1$).

We see at once that when β is near 1 or 0, the factor of $\frac{q}{RT}$ will be very small. If now q itself is also still small, as may be assumed in case of association under the influence of the molecular forces (see also Solid State VII p. 94 at the top and 98 at the bottom), we may safely neglect the correction term Δ_t in

$$f = \left(1 + \frac{a}{pv^2}\right)(1 + \Delta_t),$$

and write, just as VAN DER WAALS does:

$$f = 1 + \frac{a}{pv^2}, \quad \ldots \quad \ldots \quad \ldots \quad (10^a)$$

at least in the neighbourhood of the critical point. But we should bear in mind that strictly speaking this can never be quite exact so long as the state of association is also influenced by the temperature.

If (10^a) should practically be sufficiently accurate, we should of course also be able to calculate the quantity a from it.

Before proceeding to calculate the quantities β and φ from μ and f at the critical point, we shall first derive the value of a few quantities, which are of importance at te critical point. We mean the quantities $b' = \frac{db}{dv}$ and $-vb'' = -v\frac{d^2b}{dv^2}$. It is self-evident that we do *not* find the values now, found for this before by VAN DER WAALS and by myself. For if we start from the equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^3}$$

without the factor $1 + x\beta$ of RT, we find b' from

$$\frac{dp}{dv} = -\frac{RT(1-b')}{(v-b)^2} + \frac{2a}{v^3} = 0.$$

and b'' from $\frac{d^2p}{dv^2} = 0$, which after elimination of a and RT yields

(see also Teyler 1905: Quelques remarques sur l'equation d'ètat, p. 46) :

$$\frac{v}{v-b}(1-b') + \frac{^1/_2\,vb''}{1-b'} = \frac{3}{2}.$$

But the values of b' and b'' resulting *from this* will of course be slightly different from those which we shall now calculate from the same experimental data; and so we are not allowed to draw any conclusions from the deviation of the values of b' and b'' calculated by us just now from those found before. They remain simply secondary values, which can never be found by direct experiment, but only by the calculation *based on certain suppositions*.

Now in the first place the value of b' can be found from (3), viz. $b = b_q - (1-\beta)\Delta b$, from which directly follows :

$$b' = \frac{db}{dv} = \Delta b\,\frac{d\beta}{dv}.$$

Taking (d) and $(1 + x\beta)\dfrac{\Delta b}{v-b} = \varphi$ into account, we get :

$$b' = \frac{\dfrac{1}{x+1}\,\beta\,(1-\beta)\,\varphi\,(x+\varphi)}{1 + \dfrac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2} \qquad \ldots \ldots \quad (11)$$

The calculation of b'' from this expression is about as elaborate as that of $\dfrac{d^2p}{dv^2}$ from $\dfrac{dp}{dv}$ $\left(\text{see } \S\ 2 \text{ the calculation of } \dfrac{v_k}{v_k-b_k}\right)$. The easiest way to reach the result is the following. The numerator of the second member of (11) being $= \dfrac{\varphi}{x+\varphi}\,y$ $\left(\text{we put } y \text{ for } \dfrac{1}{x+1}\beta(1-\beta)(x+\varphi)^2\right.$

for shortness' sake, above in $\left.\S\ 2\right)$, we have :

$$b'\,(1+y) = \frac{\varphi}{x+\varphi}\,y,$$

hence

$$b''\,(1+y) + b'\,\frac{dy}{dv} = \frac{\varphi}{x+\varphi}\frac{dy}{dv} + \frac{x}{(x+\varphi)^2}\,y\,\frac{d\varphi}{dv}.$$

But as $\dfrac{\varphi}{x+\varphi} - b' = \dfrac{\varphi}{x+\varphi} - \dfrac{\varphi}{x+\varphi}\dfrac{y}{1+y} = \dfrac{\varphi}{x+\varphi}\dfrac{1}{1+y}$, we have also :

$$(v-b)\,b''\,(1+y) = \frac{\varphi}{x+\varphi}\frac{1}{1+y}(v-b)\frac{dy}{dv} + \frac{xy}{(x+\varphi)^2}(v-b)\frac{d\varphi}{dv}.$$

Now according to (ψ), we have:

$$(v - b) \frac{dy}{dv} = \frac{1}{(x+1)(1+y)} \left[- 2\beta (1 - \beta) \varphi (x + r) + \right.$$

$$+ \left. \frac{1}{x+1} \beta (1 - \beta) (1 + x\beta) (1 - 2\beta) (x + \varphi)^3 \right],$$

while according to (ε)

$$(v - b) \frac{d\varphi}{dv} = - \frac{\varphi}{1 + y}.$$

Hence:

$$(v - b) b'' (1 + y)^2 = \frac{\varphi}{x + \varphi} \left[\frac{1}{(x+1)(1+y)} \right\} - 2\beta (1 - \beta) \varphi (x + \varphi) +$$

$$+ \frac{1}{x+1} \beta (1 - \beta) (1 + x\beta) (1 - 2\beta) (x + \varphi)^3 \right\} - \frac{xy}{x + \varphi} \right],$$

or

$$(v - b) b'' (1 + y)^3 = \varphi \left[- \frac{2}{x+1} \beta (1 - \beta) \varphi + \right.$$

$$+ \frac{1}{(x+1)^2} \beta (1 - \beta) (1 + x\beta) (1 - 2\beta) (x + \varphi)^2 - \frac{xy (1 + y)}{(x + \varphi)^2} \right].$$

After substitution of

$$y (1 + y) = \frac{1}{x+1} \beta (1 - \beta) (x + \varphi)^2 + \frac{1}{(x+1)^2} \beta^2 (1 - \beta)^2 (x + \varphi)^4,$$

we get further:

$$(v - b) b'' (1 + y)^3 = \varphi \left[- \frac{1}{x+1} \beta (1 - \beta) (x + 2\varphi) + \right.$$

$$+ \frac{1}{(x+1)^2} \beta (1 - \beta) (x + \varphi)^2 \left[(1 + x\beta) (1 - 2\beta) - x\beta (1 - \beta) \right] \right],$$

hence finally (putting $(1 + y = m$, see (5)):

$$- vb'' = \frac{v}{v - b} \frac{\varphi}{m^3} \frac{1}{x + 1} \beta (1 - \beta) \left[(x + 2\varphi) + \frac{1}{x + 1} (x\beta^2 + 2\beta - 1)(x + \varphi)^2 \right]. \quad (12)$$

Finally the value of $\frac{b_k}{b_g}$ can be found from

$$b_k = b_g - (1 - \beta) \Delta b,$$

from which follows:

$$\frac{b_k}{b_g} = 1 - (1 - \beta) \frac{\Delta b}{b_g}. \quad \ldots \ldots \quad (13)$$

Of the now derived quantities only μ and f are of use for the calculation of the two unknown quantities β and φ at the critical point. Then the value of x can be assumed to be such, that we get

a suitable value of $\dfrac{\Delta b}{v-b}$ calculated from $\varphi = (1+x\beta)\dfrac{\Delta b}{v-b}$. If we wanted to consider x, β, and φ as unknown quantities, so that the value of $\dfrac{\Delta b}{v-b}$ was of course determined, the knowledge of a *third* quantity would still be required at the critical point. This third quantity could be no other than the direction of the so-called "straight diameter" in the critical point. But as the discussion of this calls for a separate study, which we hope to give in a following Paper, we shall now content ourselves with the knowledge of μ and f, and simply examine at what value of x a suitable value of $\dfrac{\Delta b}{v-b}$ is obtained with the calculated values of β and φ.

4. Let us in the first place examine what the approximate formula (10^a) for f teaches us concerning the values of the quantities m and n.

From $f = 1 + \dfrac{a}{pv^2}$ follows:

$$f - 1 = \dfrac{\dfrac{a}{v_k^2}}{p_k} = \dfrac{\dfrac{a}{b_k^2}\left(\dfrac{b_k}{v_k}\right)^2}{\dfrac{1}{27}\dfrac{a}{b_k^2}\dfrac{(3m^2-2n)^2\,(4n-3m)}{m^3}},$$

or as $\dfrac{b_k}{v_k}$ is $= \dfrac{3m^2-2n}{3m^2}$, according to (6) :

$$f - 1 = \dfrac{3m}{4n-3m}.$$

or also $\dfrac{f-1}{f} = \dfrac{3m}{4n}$, i.e.

$$\dfrac{m}{n} = \dfrac{4}{3}\dfrac{f-1}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

If we now assume a "mean" normal substance, for which the value of f may be put to be 7, we find for the ratio $m:n$ the value

$$\dfrac{m}{n} = \dfrac{8}{7}.$$

After division by $1 + x$,

$$\mu = \dfrac{3}{8}\dfrac{1+x\beta}{1+x}\dfrac{m^2}{n^2}\left(4-3\dfrac{m}{n}\right)n \quad . \quad . \quad . \quad . \quad . \quad (b)$$

follows from (9), as we shall regard the value of v_k in $\dfrac{p_k v_k}{RT_k}$ as referring to simple molecular quantities.

With $\dfrac{m}{n} = \dfrac{8}{7}$ it follows from this that

$$n = \frac{343}{96} \frac{1+x}{1+x\beta} \mu.$$

If in this we substitute the value 0,265 for μ, which value about agrees with our substance for which $f = 7$, we get:

$$n = 0,947 \frac{1+x}{1+x\beta} \; ; \quad m = \frac{8}{7} n \quad . \quad . \quad . \quad . \quad . \quad (c)$$

As according to (5)

$$n = 1 + \frac{3x}{2(x+1)} \beta (1-\beta) \cdot (x+\varphi) +$$

$$+ \frac{1}{2(x+1)^2} \beta (1-\beta) (1+2 (x-1) \beta - 3x\beta^2) (x+\varphi)^3 \Bigg\}, \quad (5)$$

$$m = 1 + \frac{1}{x+1} \beta (1-\beta (x+\varphi)^2$$

we can find the values of β and φ from the above equations with an arbitrary value of x.

Thus e.g. with $x = 1$ we find the values:

$$\underline{\beta = 0,9547; \quad \varphi = 1.227.}$$

For then n becomes $= 0,947 \times \dfrac{2}{1,955} = 0,969; m = \dfrac{8}{7} n = 1,107,$ while

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

$$= 1 + \frac{3}{4} \times 0,04325 \times 2,227 - \frac{1}{8} \times 0,04325 \times 1,7344 \times (2,227)^3$$

$$= 1 + 0,0722 - 0,1036 = 0,969.$$

also follows from (5).

And as to m:

$$m = 1 + \frac{1}{2} \beta (1-\beta) (1+\varphi)^2 = 1 + \frac{1}{2} \times 0,04325 \times (2,227)^2$$

$$= 1 + 0,1072 = 1,107.$$

Then we find further the value $\dfrac{1.227}{1,955} = 0,628$ for $\dfrac{\Delta b}{v-b}$ from

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

This value is probably too high. For if we put $\dfrac{v_k}{b_k}$ at about 2,1, then $v_k = 8,4 \varrho$, because b_k is by approximation about equal to $b_q = 4\varrho$ ($\varrho =$ the volume proper of the molecules). Hence the limiting volume b_a for $v = b$ ($=$ that of the complex molecules b_1) is about

$\dfrac{1}{4} \times 8,4 \varrho = 2,1 \varrho$, because in most cases a value is found for this limiting volume in the neighbourhood of $^1/_4$ of the critical volume.

As now $b_g = v b_2 = 4\varrho$ and $b_a = b_1 = 2,1\varrho$, so $\Delta b = - b_1 +$ $+ v b_2 = 1,9\varrho$, and hence

$$\frac{\Delta b}{b_g} = \frac{1,9}{4} = 0,475.$$

So we find for $\dfrac{\Delta b}{v - b}$, supposing $\dfrac{\Delta b}{b_k} = \dfrac{\Delta b}{b_g}$:

$$\frac{\Delta b}{v_k - b_k} = \frac{\dfrac{\Delta b}{b_k}}{\dfrac{v_k}{b_k} - 1} = \frac{0,475}{2,1 - 1} = 0,43.$$

So the value 0.63, which we found above, is too high. But we must not attach too much importance to this circumstance, because it is very well possible that at lower temperatures and smaller volumes, where association to molecule-complexes which are larger on an average, will take place, and x accordingly assumes a higher value, φ will *naturally* decrease. We pointed out already above that the quantity x is properly speaking, variable, and that we should only consider it to be constant provisionally in the neighbourhood of the critical point to simplify the considerations.

Before we proceed, however, and repeat the foregoing calculation for $x = 2$, we shall first calculate the relation $\dfrac{v_k}{b_k}$ with the values found for m and n, and also the factors of $\dfrac{8}{27}\dfrac{a}{b_k}$ and $\dfrac{1}{27}\dfrac{a}{b_k^2}$ resp. in the expressions for RT_k and p_k. We have viz. according to (6):

$$\frac{v_k}{b_k} = \frac{3m^2}{3m^2 - 2n} = \frac{3 \times (1,107)^2}{id - 2 \times 0,969} = \frac{3,678}{1,740} = \underline{2,114.}$$

So we see that the ordinary theory of association, though β differs only little from 1, and in consequence m and n only deviate little from 1, is perfectly adequate to account for the very considerable diminution of the ratio $v_k : b_k$ from 3 to about 2,1, a value which is in perfect harmony with the value computed by different investi-

cators led by other considerations. Thus we may say that the values of β and φ, which we originally calculated from $f = 7$ and $\mu = 0,265$ are also *reversely* able, to reduce $v_k : b_k$ from 3 to 2,1, f from 4 to 7, and μ from 0,375 to 0,265. The ordinary theory of the apparent diminution with the coefficients α, β, etc. in the expression $b = b_q \left(1 - \alpha \dfrac{b_q}{v} + \beta \left(\dfrac{b_q}{v} \right)^2 - \text{etc.} \right)$ has always failed to do this, (see also TEYLER, 1901, "Sur l'influence des corrections etc.", p. 1—10, specially p. 10 at the top).

If in formula (7) a and b_k are made to refer to simple molecular quantities, the second member has to be multiplied by the factor $1 + x \, (= v)$, and we get:

$$RT_k = \frac{1+x}{1+x\beta} \frac{8}{27} \frac{a}{b_k} \frac{n^2 \, (3m^2 - 2n)}{m^5}.$$

So if we put $= f_1$ the factor of $\dfrac{8}{27} \dfrac{a}{b_k}$, we find for $x = 1$, as $\dfrac{n^1}{m} = \dfrac{7}{8}$:

$$f_1 = \frac{2}{1,955} \times \left(\frac{7}{8} \right)^2 \frac{3 \times (1,107)^2 - 2 \times 0,969}{(1,107)^3},$$

hence

$$f_1 = 1,023 \times \frac{49}{64} \times \frac{1,740}{1,357} = \underline{1,004.}$$

This is in perfect accordance with v. D. WAALS' observation, that — even if $v_k = 2,1 \, b_k$ instead of $3 b_k$ — RT_k yet becomes again $= \dfrac{8}{27} \dfrac{a}{b_k}$ with a high degree of approximation.

Further we have, according to (8):

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

and thus the factor of $\dfrac{1}{27} \dfrac{a}{b_k^2}$ becomes:

$$f_2 = \frac{(1,740)^2 \times 0,5536}{1,226 \times 1,357} = \frac{1,676}{1,664} = \underline{1,007.}$$

Here too it appears once more, that p_k remains $= \dfrac{1}{27} \dfrac{a}{b_k^2}$ approximately.

Clarens, Aug. 22 1911.   (To be continued).

Chemistry. — "*On the benzenehexachlorides and their splitting up into trichlorebenzenes*". By Dr. T. VAN DER LINDEN. (Communicated by Prof A. F. HOLLEMAN).

(This communication will not be published in these Proceedings).

———————

(October 26, 1911).