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Citation:

J.J. van Laar, Some difficulties and contradictions met with in het drawing up of the equation of state, in:

KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 44-59

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## **Physics.** — "Some difficulties and contradictions met with in the drawing up of the equation of state." By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

## (Communicated in the meeting of April 25, 1913).

1. The latest papers by VAN DER WAALS on the equation of state  $^{1}$ ) - also in connection with my own recent investigations  $^{2}$ ) - induce me to publish the following remarks, which may not be entirely devoid of interest at the present stage of the question.

When we start from van der WAALS's fundamental equation, viz.

and for the present disregard association or quasi-association, there are — the chosen form of the equation of state being retained — only two possibilities for the explanation of the found deviations from the above equation:

The quantity b is still a function of v (and possibly of T).

,, ,, a ,, ,, ,, ,, ,, v, or of T.

If at first we still disregard the variability with the temperature, we shall in the first place ascertain the consequences of the variability of b with v.

If b = f(v), the above equation of state gives at the critical point:

$$\begin{pmatrix} \frac{dp}{dv} \\ \frac{dv}{dv} \\ t = -\frac{RT}{(v-b)^3} (1-b') + \frac{2a}{v^3} = 0 \\ \begin{pmatrix} \frac{d^3p}{dv^3} \\ t = \frac{2RT}{(v-b)^3} (1-b')^3 + \frac{RT}{(v-b)^3} b'' - \frac{6a}{v^4} = 0 \end{pmatrix}$$

where b' is written for  $\frac{db}{dv}$ , and b'' for  $\frac{d^{2}b}{dv^{2}}$ .

Hence it follows from this that

$$RT_{k} (1 - b'_{k}) = \frac{2a(v_{k} - b_{k})^{2}}{v_{k}^{3}}$$

$$RT_{k} \left[ 2 (1 - b'_{k})^{2} + (v_{k} - b_{k}) b''_{k} \right] = \frac{6a (v_{k} - b_{k})^{3}}{v_{k}^{4}}$$

<sup>1</sup>) These Proc. Vol. XV, 903-910; XV, p. 971-981; XV, p. 1131-1145. (To be cited as v. d. W I, II, and III).

<sup>&</sup>lt;sup>9</sup>) These Proc. Vol. XIV, p. 278-298; XiV, p. 428-442; XIV, p. 563-579; XIV, p. 711-724. (To be cited as v. L. I, II, III and IV). Further XIV, p. 771-781; XIV, p. 1091-1107. (To be cited as v. L. A and B.)

Division gives:

$$3\frac{v_k-b_k}{v_k}=2(1-b'_k)+(v_k-b_k)\frac{b''_k}{1-b'_k},$$

hence, putting  $v_k b''_k : (1 - b'_k) = \beta''_k$ :

$$\frac{v_k-b_k}{v_k}=\frac{2(1-b'_k)}{3-\beta''_k}.$$

With  $\frac{v_k}{b_k} = r$ , we get finally:

Further follows from the first of the above equations for  $RT_k$ :

$$RT_{k} = \frac{a}{b_{k}} \cdot \frac{2b_{k}(v_{k}-b_{k})^{2}}{v_{k}^{3}(1-b'_{k})},$$

hence :

$$RT_k = \frac{a}{b_k} \cdot \frac{1}{r} \left(\frac{r-1}{r}\right)^2 \frac{2}{1-b'_k} = \frac{8}{27} \lambda_1 \frac{a}{b_k} \cdot \cdot \cdot \cdot (3)$$

We find finally for  $p_k$  from the equation of state by substitution of the value of  $RT_k$ :

$$p_{k} = \frac{a}{v_{k}^{3}} \frac{2(v_{k} - b_{k})}{1 - b'_{k}} - \frac{a}{v_{k}^{2}} = \frac{a}{v_{k}^{2}} \left[ \frac{v_{k} - b_{k}}{v_{k}} \frac{2}{1 - b'} - 1 \right],$$

i.e.

$$p_{k} = \frac{a}{b_{k}^{2}} \cdot \frac{1}{r^{2}} \left[ \frac{r-1}{r} \frac{2}{1-b'_{k}} - 1 \right] = \frac{1}{27} \frac{\lambda_{2}}{b_{k}^{2}} \frac{a}{b_{k}^{2}} \cdot \cdot \cdot \cdot (4)$$

Then  $(v_k = rb_k)$ :

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is found for the quantity  $s = \frac{RT_k}{p_k v_k}$ .

If therefore  $b'_k$  and  $b''_k$  are known, r is given by (2), and further  $RT_k$ ,  $p_k$ , and s by (3), (4), and (5). Reversely  $b'_k$  and  $b''_k$  can be calculated when r and s are known.

Thus e.g. with s = 3,774 (1:s = 0,265) and r = 2,11 from (5) as then (r-1): r = 0,526 and  $(r-1)^2: r^2 = 0,277$  — for  $2: (1-b'_k)$ we find the value 2,21, hence  $b'_k = 0,094$ . From (2) we then calculate further  $\beta''_k = -0,44$ , i.e.  $v_k b''_k = -0,40$ . For  $\lambda_1$  and  $\lambda_2$  we then find from (3) and (4)  $\underline{\lambda_1 = 0.98}$ , and also  $\lambda_2 = 0.98$ .

Remark. The values of  $\lambda_1$  and  $\lambda_2$  found, change only very little when association or quasi association is assumed. Then the expressions for  $r = v_k : b_k$ ,  $RT_k$ ,  $p_k$  and s, indeed, become more intricate (cf. Van L. I and II), and we shall among others find — according as partial (very slight) association to *double* molecules is assumed, or association to *triple* ones — in which the quantity *b* changes *in consequence* of this association (loc. cit. I, p. 295—297; II, p. 428—431):

r	<sup>b'</sup> k	-v <sub>k</sub> b" <sub>k</sub>	λ	λ2	$\alpha_k$
2.114	0.0534	0.295	1.004	1.007	0.977 '
2.102	0.0319	0.196	1.010	1.019	0.972

out the values of  $\lambda_1$  and  $\lambda_2$  remain in the immediate neighbourhood of unity; that of  $\lambda_1$  on an average 1,007, and that of  $\lambda_2$  on an average 1,013; i.e. they are about  $1^{\circ}/_{\circ}$  above unity, whereas when the association is disregarded, they remain about  $2^{\circ}/_{\circ}$  below it.

For  $b'_k$  and  $-v_k b''_k$  lower values, viz. the mean values 0,043 and 0,25 are found when association is assumed; whereas 0,094 and 0,40 are found, when association is left out of account.

As appears from the above values of the factor  $a_k$  of  $RT_k$  (resp.  $= (1 + \beta_k : 2 \text{ or } (1 + 2\beta_k) : 3)$ , the association at the critical pointis still exceedingly slight'); the mean value of  $a_k$  being = 0.975, on an average only  $2^1/_2$  % of the simple molecules have aggregated to multiple ones.

On this occasion, in connection with the footnote on p. 178 in the cited paper by KAMERLINGH ONNES and KEESOM, we may remind of the fact that according to my considerations there would indeed be double and triple molecules in the neighbourhood of the critical temperature — but only to an exceedingly slight amount, viz. about  $2^{1}/_{2}^{0}/_{0}$  (see above).

<sup>&</sup>lt;sup>1</sup>) In their interesting and thorough paper on the equation of state in the Encyklopädie der Math. Wiss. (12 Sept. 1912, p 615-945) KAMERLINGH ONNES and KEESOM make the very true remark on p. 177 (paging of the reprint in the "Comm."), that it is going too far to ascribe every deviation from the ideal equation of state to association. Also my statement in the TEYLER-paper cited there, is too sweeping in this respect. It appears sufficiently from the above remarks that the simple assumption of the variability of b with v can also satisfactorily account for these deviations (see also § 2). It remains of course to be seen to what this variability of b is due: in a quasi or in a real diminution of the volume of the molecules (v. D. WAALS) — or in a variation of b also in consequence of the association (v. L. I and II).

Also the value of r, viz. 2,11 on an average, remains in the neighbourhood of 2,1, the value found for it experimentally.

I calculated all these values then not from those of s and r, but from those of s and f, viz. s = 3,774, f = 7.

It is seen that the assumption of possible *association* does not bring a *real change* in the\_values of the *critical* quantities (determined by r,  $\lambda_1$ , and  $\lambda_2$ ) — and may therefore be left out of account in their determination.

Another *Remark.* We put  $v_k : b_k = r$  in the above, and  $not v_k : b_g$ (v. d. W. l. c.). In the expressions for the critical quantities namely  $b_k$  occurs, and not  $b_g$  — and therefore to get more certainty in the formulae, and to remain independent of the theoretically and experimentally somewhat unwieldy relation  $b_g : b_k$ . I have thought I ought to introduce  $b_k$  and not  $b_g$  into the formulae (cf. v. L. A., p. 772). [According to the association theory, see v. L. II, p. 422 and 431,  $b_g : b_k$  is resp. = 1,03 or = 1,015 according as partial association (to an amount of on an average only about  $2^{1/2} o_{0}$ , see above) to double or to triple molecules is assumed].

There is another advantage in putting  $v_k : b_k = r$ , namely this that now the factors  $\lambda_1$  and  $\lambda_2$  in the formulae (3) and (4) for  $RT_k$  and  $p_k$  are much nearer unity than when  $b_q$  is introduced. For both for  $RT_k$  and for  $p_k$  (leaving the factor r-1 out of account)  $r = v_k : b_k$  occurs to the *third* power, so that the deviation of the ratio  $b_g : b_k$  from unity will be found in  $\lambda_1$  and  $\lambda_2$  at least *three times enlarged*. If therefore according to VAN DER WAALS  $b_g : b_k = 1,04$ à 1,05, or according to the above 1,015 à 1,03<sup>-1</sup>), hence on an average about 1,03,  $\lambda_1$  and  $\lambda_2$  can differ about 10°/<sub>0</sub> from unity when  $r' = v_k : b_g$  is assumed instead of  $r = v_k : b_k$ , and the relations drawn up by VAN DER WAALS between r, s, and f will be valid only by approximation, whereas they may be considered as almost entirely accurate when  $r = v_k : b_k$  is introduced.

1) As  $rs = 8 \frac{\lambda_1}{\lambda_2}$ ,  $b_g : b_i$  may be determined from:  $b_g = r - rs = \lambda_1$ 

 $\frac{b_q}{b_k} = \frac{r}{r'} = \frac{rs}{r's} = 8\frac{\lambda_1}{\lambda_2}: r's,$ 

when  $r' = v_k : b_g$  is known from experiment.

As  $\frac{r-1}{r} = \frac{s}{f}$  or  $r\left(1 - \frac{s}{f}\right) = 1$  follows from (6) — see § 2 — also  $r'\left(1 - \frac{s}{f}\right) = \frac{r'}{r} = \frac{b_k}{b_q}$ , from which the relation  $b_g : b_k$  may also be determined. [When association is taken into account, the factor  $\alpha_k$  is added to s].

**2**. The quantity f. Relations between f, r, and s. When neither a nor b is a function of T, it follows from (1) that

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b}$$
, or  $= \frac{1}{T}\left(p + \frac{a}{v^2}\right)$ ,

and so also:

$$\frac{T}{p}\left(\frac{dp}{dT}\right)_{v} = \frac{RT}{p(v-b)}, \text{ or } = 1 + \frac{a}{pv^{2}}.$$

At the critical point  $\left(\frac{dp}{dT}\right)_{v} = \left(\frac{dp}{dT}\right)_{coix.} \frac{dp}{dT}$ , so that there

$$f = \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = \frac{RT_k}{p_k(v_k - b_k)} = s \frac{v_k}{v_k - b_k}, \text{ or } = 1 + \frac{a}{p_k v_k^2}$$

After substitution of the value s from (5),  $p_k$  from (4), and  $v_k = rb_k$ , we get:

If in the second relation according to (5) we substitute  $\frac{s^2}{64} \left(\frac{\lambda_2}{\lambda_1}\right)^2$ 

for 
$$\frac{1}{r^3}$$
, then

As r no longer occurs in this, VAN DER WAALS was justified in saying that this equation derived by him, viz.  $\frac{f-1}{s^2} = \frac{27}{64}$ , would be almost entirely exact, whereas the two others, viz, (5) and (6) with  $r' = v_k : b_g$ , would only be true by approximation. But as we already observed above, when not r' but  $r = v_k : b_k$  is taken, these latter equations too will hold with the same degree of accuracy as (7).

As, when association is disregarded,  $\lambda_1 = 0.977$  and  $\lambda_2 = 0.980$ ; whereas, when it is taken into account, on an average  $\lambda_1 = 1.007$ ,  $\lambda_2 = 1.013$ , the ratio  $\lambda_1 : \lambda_2$  will be = 1 - 0.003 or = 1 - 0.006in (5) and (6), i.e. it may be put equal to unity. For  $\lambda_2 : \lambda_1^2$  we find 1.026 or 1.001, so that this ratio approaches unity still more closely than  $\lambda_1 : \lambda_2$  on assumption of association, but with disregard of it will not differ more from unity than 2 or  $3^{\circ}/_{\circ}$ . Finally  $1 : \lambda_2$ in the second equation (6) will remain either  $2^{\circ}/_{\circ}$  above, or about  $1^{\circ}/_{\circ}$  below unity.

The value 2,11 is found for r from (5) with s = 3,774, while the second equation (6) with f = 7 also yields the value 2,11. Further  $s^2: (f-1) = 14,24: 6 = 2,37$ , and also 64: 27 = 2,37; so that equation (7) is accurately satisfied with these values of s and f.

With regard to the first equation (6) it should be borne in mind that when association is taken into account, a factor  $\alpha_k$  appears in the second member. (because then f becomes  $= \alpha_k RT_k : p_k (v_k - b_k)$ . Thus :

$$f = \alpha_k \, s \frac{r}{r-1} = \frac{8}{r-1} \, \alpha_k \frac{\lambda_1}{\lambda_2},$$

in which according to the table in §1  $\alpha_k$  has the mean value of 0,975. (cf. also v. L. A., p. 772). From

$$f - 1 = \frac{27}{r^2} \frac{1}{\lambda_2} \quad ; \quad \frac{f - 1}{s^2} = \frac{27}{64} \frac{\lambda_2}{\lambda_1^2}$$

r and s may be expressed in f-1, and we find then:

$$r = \frac{3}{\sqrt{\frac{f-1}{3}\lambda_2}} ; \quad s = \frac{8}{3}\sqrt{\frac{f-1}{3}\frac{\lambda_1}{\lambda_2}}, \quad \dots \quad (8)$$

two relations also derived by VAN DER WAALS, — but now, the factors  $\lambda_1$  and  $\lambda_2$  having been taken into account, quite accurate.

Putting  $\lambda_1$  and  $\lambda_2 = 1$ , we find from this approximately, when f = 7:

$$r = \frac{3}{\sqrt{2}} = 2,12$$
;  $s = \frac{8}{3}\sqrt{2} = 3,77.$ 

That the factor  $\bigvee 2$  plays a part, I had already surmised before, without knowing the cause. See inter alia the Vorlesungen über theoretische und physik Chemie by VAN 'T HOFF, 3<sup>es</sup> Heft, p. 14, and the Vorwort p. VI (1900). Besides already in 1905 (Arch. TEYLER) I expressed some critical quantities in experimentally determinable quantities in a perfectly analogous way as later VAN DER WAALS — however with the exclusion of the quantity f, as the possibility that b and particularly a could be functions of the temperature, was not excluded by me. (Cf. also v. L. A., p. 773).

## **3.** Difficulties and objections.

So far there is not a single objection, and if there were no other characteristic critical quantities than r, s, and f, it would suffice to consider b as function of v, and to seek the cause of this variability. The association (or quasi-association) might then be accepted or left as a gratuitous addition. It would not be necessary.

But unfortunately, matters are different. There is namely one more characteristic quantity, i.e. the quantity  $\varphi$ , given by

$$\varphi = \frac{F-1}{F_k-1} \frac{\varepsilon}{d_1 d_2},$$

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in which  $F = \frac{T}{p} \frac{dp}{dT}$ ,  $F_k = \left(\frac{T}{p} \frac{dp}{dT}\right)_k$ ,  $\epsilon = \frac{p}{p_k}$ ,  $d_1 = \frac{v_k}{v_1}$ ,  $d_2 = \frac{v_k}{v_2}$ . Here p

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denotes the pressure of coexistence,  $v_1$  and  $v_2$  the specific volumes of the coexisting liquid and vapour phases.

If only b = f(v),  $\varphi$  would be = 1 at all temperatures, and not only at the critical temperature. But as it has been found that  $\varphi$ increases from 1 to about 1.4, when the temperature falls from  $T_k$ to about  $1/{_2} T_k$  (cf. also v. D. W. loc. cit., and v. L. B., p. 1100—1101) — it follows that necessarily either a must contain a function of v, besides  $1:v^2$ , or a (or also b) must still be a (non-linear) function of T.

VAN DER WAALS thought he could allow for this by putting

$$a \equiv a_0 (1 - \frac{1}{2}x)^2$$
,

in which x represents the relative number of quasi-associated molecules. Since besides on T, x will depend on v in a high degree, a function of v has been applied here to a. The dependence of the temperature may be neglected, as in case of (quasi) association under the influence of the molecular forces the generation of heat may be put = 0 (cf. also v. p. W. loc. cit., and v. L. I, p. 291; A, p. 771)

But apart from the insufficient justification of the above relation in my opinion, especially as far as the coefficient 1/2 (in general = 1-k) is concerned — it will be shown in what follows that every function  $\theta = f(v)$  for  $a/v^2$  will lead to contradictions, when it would have to account for the great decrease of the quantity  $\varphi$  in the immediate neighbourhood of the critical temperature, while at the same time f = 7, r = 2,1 and s = 3,8 remain. The said decrease is so considerable at  $T_k$ , that  $\left(\frac{d\varphi}{dm}\right)_k$  may be put = -7 ( $m = T: T_k$ ; cf. v. L. B, p. 1101 et seq.)

We therefore put e.g.  $a = a_k \theta$ , in which  $\theta = f(v : v_k)$ . The quantity a may therefore be for some reason or other (e.g. quasi association, see above) a function of v — and hence in case of coexistence of two phases also *indirectly* of T.

The *direct* dependence on T, which we shall discuss later, is left entirely out of account for the present.

From

follows in a quite analogous way as was derived above in § 1:

$$\begin{pmatrix} \frac{dp}{dT} \end{pmatrix}_{v} = -\frac{RT}{(v-b)^{2}} (1-b') - a_{k} \left( -\frac{2\theta}{v^{3}} + \frac{\theta'}{v_{k}v^{2}} \right) = 0$$

$$\begin{pmatrix} \frac{d^{2}p}{dT^{2}} \end{pmatrix}_{v} = \frac{2RT}{(v-b)^{3}} (1-b')^{2} + \frac{RT}{(v-b)^{2}} b'' - a_{k} \left( \frac{6\theta}{v^{4}} - \frac{4\theta'}{v_{k}v^{3}} + \frac{\theta''}{v_{k}^{2}v^{2}} \right) = 0$$

$$\text{ when } \theta' = \frac{d\theta}{v^{4}} \text{ and } \theta'' = \frac{d^{2}\theta}{v^{2}} \quad (v = v, w)$$

when 
$$\theta' = \frac{d\theta}{dn}$$
 and  $\theta'' = \frac{d\theta}{dn^2}$  .-  $(n = v : v_k)$ .

Hence:

$$RT_{k} (1-b'_{k}) = \frac{2a_{k}(v_{k}-b_{k})^{2}}{v_{k}^{3}} (\theta_{k}-1/2\theta'_{k})$$

$$RT_{k} \left[ 2(1-b'_{k})^{2} + (v_{k}-b_{k})b''_{k} \right] = \frac{6a_{k}(v_{k}-b_{k})^{3}}{v_{k}^{4}} \left( \theta_{k}-1/2\theta''_{k} - \theta_{k} + 1/2\theta''_{k} \right)$$

yielding by division:

$$3\frac{v_k-b_k}{v_k} = \frac{2(1-b'_k)+(v_k-b_k)\frac{b''_k}{1-b'_k}}{(1-2^{2}/2\theta'_k+1/2\theta''_k):(1-2^{2}/2\theta'_k)},$$

as  $\theta_k$  apparently = 1.

With  $v_k : b_k = r$ ,  $v_k b''_k : (1 - b'_k = \beta''_k, (1 - \frac{3}{3}\theta'_k + \frac{1}{6}\theta''_k) : (1 - \frac{1}{2}\theta'_k) = \omega$ we get:

$$\frac{r-1}{r} (3\omega - \beta''_k) = 2 (1 - b'_k),$$

 $\mathbf{or}$ 

$$\frac{r-1}{r} = \frac{2}{3} \frac{1-b'_k}{\omega - \frac{1}{s} \beta''_k}, \quad \dots \quad \dots \quad (2a)$$

so that (2*a*) differs from (2) only in this, that now  $\omega - \frac{1}{s} \beta''_k$  occurs in the denominator instead of  $1 - \frac{1}{s} \beta''_k$ .

We now find for  $RT_k$  and  $p_k$ :

$$RT_{k} = \frac{a_{k}}{b_{k}} \cdot \frac{1}{r} \left( \frac{r-1}{r} \right)^{*} \frac{2 \left( 1 - \frac{1}{2} \theta'_{k} \right)}{1 - b'_{k}} \quad . \quad . \quad . \quad (3a)$$
$$a_{k} \quad 1 \quad | \ r-1 \quad 2 \left( 1 - \frac{1}{2} \theta'_{k} \right) \quad . \quad . \quad . \quad . \quad (3a)$$

$$r^{j_{k}} = \frac{a_{k}}{b_{k}^{*}} \cdot \frac{1}{r^{2}} \left[ \frac{r-1}{r} \frac{2(1-r_{j_{2}}O_{k})}{1-b'_{k}} - 1 \right], \quad . \quad . \quad (4a)$$

s becoming:

$$s = \frac{\left(\frac{r-1}{r}\right)^{2} \frac{2\left(1-\frac{1}{2}\theta'_{k}\right)}{1-b'_{k}}}{\frac{r-1}{r} \frac{2\left(1-\frac{1}{2}\theta'_{k}\right)}{1-b'_{k}} - 1}.$$
 (5a)

In this the factor  $1 - \frac{1}{2}O'_k$  always occurs as a multiplicator of  $2:(1-b'_k)$ .

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So with s = 3,774 and r = 2,11 we now find the value 2,21 for  $2(1-\frac{1}{2}\theta'_k): (1-\frac{b'_k}{2})$ , i. e.  $(1-\frac{1}{2}\theta'_k): (1-\frac{b'_k}{2}) = 1,105$ . And as  $b'_k$  has a very small positive value,  $\theta'_k$  will necessarily have a very small (probably negative) value. But then  $\theta''_k$  must possess a very great positive value, viz. about 2,7, if  $\left(\frac{d\varphi}{dm}\right)_k$  is to become = -7 (see above), as we shall show now.

We namely derived before (v. L. B, p. 1098, formulae (4) and (5)):

$$\varphi = \frac{F-1}{F_L-1} \frac{\varepsilon_{cocz.}}{d_1 d_2} = 1 + \lambda (1-m) + \ldots,$$

in which

$$\lambda = (\alpha^2 - 2\beta) - \frac{F'_k}{F_k - 1} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (9)$$

In this  $F'_k$  represents  $\left(\frac{d^2 \varepsilon_{ccer.}}{dm^2}\right)_k$ , while  $\alpha$  and  $\beta$  are the first coefficients of the expansion into series.

$$d_1 = 1 + \alpha \sqrt{1-m} + \beta (1-m) + \dots$$
  
$$d_2 = 1 - \alpha \sqrt{1-m} + \beta (1-m) - \dots$$

given by (see p. 1094 and 1096 loc. cit.)

$$\alpha = \sqrt{\frac{6\varepsilon''_{v,t}}{\varepsilon'''_{v^3}}}; \quad \beta = \alpha^2 - \frac{\varepsilon'''_{v^2,t} - \frac{1}{10}\alpha^2\varepsilon'''_{v^4}}{\varepsilon'''_{v^3}}.$$

In this  $\varepsilon''_{v,t}$  stands for  $\left(\frac{d^3\varepsilon}{dn \cdot dm}\right)_k$ ,  $\varepsilon'''_{v^2,t}$  for  $\left(\frac{d^3\varepsilon}{dn^3 \cdot dm}\right)_k$ ,  $\varepsilon'''_{v^3}$  for

 $\left(\frac{d^3\varepsilon}{dn^3}\right)_k$ , and  $\varepsilon'''_{n^4}$  for  $\left(\frac{d^4\varepsilon}{dn^4}\right)_k$ . The quantities  $\varepsilon$ , m, and n are resp. the reduced pressure, temperature, and volume.

Now taking the value of  $F'_k$ , viz. (see p. 1098 and 1104 loc. cit.)  $F'_k = \varepsilon''_{\ell'} - (\alpha^2 - \beta) \varepsilon''_{\nu,t} - \frac{1}{\sigma} \alpha^2 \varepsilon''_{\nu^2,t}$  into account, we may also write for :

$$\lambda = \frac{-\epsilon''_{t^2} + \alpha^2 \left[ (f-1) + \epsilon''_{v,t} + \frac{1}{4} \epsilon'''_{v^2,t} \right] - \beta \left[ 2(f-1) + \epsilon''_{v,t} \right]}{f-1}, \quad (9a)$$

in which  $\varepsilon''_{\ell^2} = \left(\frac{d^2\varepsilon}{dm^2}\right)_k$ , i. e. for n(v) constant. (so  $\varepsilon$  not the reduced pressure of coexistence). For  $F_k$  we haven written f (see § 2).

We now find — as  $\lambda = -\left(\frac{d\varphi}{dm}\right)_k$  — the value 7 (at the least 6,8 loc. cit. p. 1101) for this quantity  $\lambda$ .

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Let us now calculate the different differential quotients of  $\varepsilon$  with respect to m and n with the aid of (1a). We find:

$$\begin{pmatrix} \frac{dp}{dT} \end{pmatrix}_{v} = \frac{R}{v - b} = \frac{1}{T} \left( p + \frac{a_{k}\theta}{v^{2}} \right); \quad \left( \frac{d^{2}p}{dT^{2}} \right)_{v} = 0$$

$$\frac{d^{2}p}{dvdT} = \frac{1}{T} \left[ \frac{dp}{dv} + a_{k} \left( -\frac{2\theta}{v^{3}} + \frac{\theta'}{v_{k}v^{2}} \right) \right]$$

$$\frac{d^{3}p}{dv^{2}dT} = \frac{1}{T} \left[ \frac{d^{2}p}{dv^{2}} + a_{k} \left( \frac{6\theta}{v^{4}} - \frac{4\theta'}{v_{k}v^{3}} + \frac{\theta''}{v^{2}_{k}v^{2}} \right) \right].$$

Hence for  $T_k$   $\left(\theta_k = 1, \frac{dp}{dv} = 0, \frac{d^3p}{dv^2} = 0\right)$ :  $t = \frac{T_k}{dv} \left(\frac{dp}{dv}\right) = 1 + \frac{a_k}{dv} = s^{p_k} = t^{p_k}$ 

$$f = \frac{v}{p_k} \left(\frac{1}{dT}\right)_k = 1 + \frac{v}{p_k v^2_k}; \quad \varepsilon''_{\ell^2} = 0$$
$$\varepsilon''_{\nu,\ell} = \frac{v_k T_k}{p_k} \left(\frac{d^2 p}{dv dT}\right)_k = \frac{a_k}{p_k v^2_k} (-2 + \theta'_k)$$
$$\varepsilon'''_{\nu^2,\ell} = \frac{v^2_k T_k}{p_k} \left(\frac{d^2 p}{dv^2 dT}\right)_k = \frac{a_k}{p_k v^2_k} (6 - 4\theta'_k + \theta''_k).$$

So we find for  $\lambda$ :

$$\lambda = a^{2} \left[ 1 + (-2 + \theta'_{k}) + \frac{1}{6} (6 - 4\theta'_{k} + \theta''_{k}) \right] - \beta \left[ 2 + (-2 + \theta'_{k}) \right],$$

i. e.

$$\lambda = \alpha^{2} \left( \frac{1}{3} \theta'_{k} + \frac{1}{6} \theta''_{k} \right) - \beta \theta'_{k}.$$

As experimentally about (see also v. L. B, p. 1101):

$$a^3 = 15;$$
  $\beta = 0.9;$   $\lambda = 6.8$ 

has been found, we get:

$$4,1 \,\theta'_k + 2,5 \,\theta''_k = 6,8.$$

Hence if  $\theta'_k$  is very small — which is inevitable according to (5a) (see above) —  $\theta''_k$  will necessarily have to lie in the neighbourhood of 2,7 (with  $\theta'_k = -0,1$ ,  $\theta''_k$  would be found even 2,9). We may therefore consider the value 2,7 as the *lowest* required to make  $\lambda = 6.8$ , as no doubt  $\theta'_k$  will always have a negative value, even though it be a very small one (see above).

Granting this to be true — and it is hardly possible to deny the above, when for the equation of state the form (1a) is assumed with b and a as functions of v — it is easy to see that the result found leads to a *perfectly impossible* result for  $b''_k$ , if the critical volume etc. must also have the desired experimental value.

For from (2a), viz.

$$\frac{r-1}{r} = \frac{2}{3} \frac{1-b'_k}{\omega - \frac{1}{s} b''_k},$$

with r = 2,1 and  $b'_k$  small, e.g. = 0,04 — since the value of  $\omega = (1-\frac{2}{3}\theta'_k + \frac{1}{6}\theta''_k): (1-\frac{1}{2}\theta'_k)$ 

will amount to about =  $1 + \frac{1}{6} \times 2.7 = 1.45$  — will follow:  $\beta''_{k} = 0.69$ , i. e.  $v_{k}b''_{k} = 0.66$ .

So instead of finding a *negative* value, which varies according to the different assumptions from -0,40 to -0,20 (-0,40 when association is not assumed), we now find an impossibly large positive value for  $v_k b''_k$ .

And as nobody will think possible the fantastical course of the quantity b following from this, any attempt to account for the course of the characteristic quantity  $\varphi$  in the neighbourhood of  $T_k$ , where  $\frac{d\varphi}{dm} = -7$ , — while at the same time the ordinary quantities must retain their known experimental values — by the addition of a factor  $\theta = f(v)$  by the side of  $a/v^2$  — hence also of VAN DER WAALS'S factor  $(1-\frac{1}{2}x)^2$ , in which x is a function of v — should be rejected. In this state of affairs there is nothing left but to assume *direct* 

dependence of the quantities a or b on the temperature.

4. The quantities a or b are functions of the temperature. When a or b are temperature-functions, all the relations derived in § 1. remain unchanged at the critical point, because in their derivation we only differentiated with respect to v with T constant.

But the value of f, derived in § 2, will in general undergo a change. a. When **a** is a temperature-function, we may put  $a = a_k \tau$ , in which  $\tau = f\left(\frac{T}{T_k}\right)$ . From

follows, when  $\frac{d\mathbf{r}}{dm}(m = T: T_k)$  is represented by  $\mathbf{r}'$ :

$$\left(\frac{dp}{dT}
ight)_v = rac{R}{v-b} - rac{a_k \, oldsymbol{ au}'}{T_k \, v^2}, \ \mathrm{or} \ = rac{1}{T} \left(p + rac{a_k \, oldsymbol{ au}}{v^2}
ight) - rac{a_k \, oldsymbol{ au}'}{T_k \, v^2}.$$

Hence also:

$$\frac{T}{p}\left(\frac{dp}{dT}\right)_{v} = \frac{RT}{p(v-b)} - \frac{Ta_{k}\mathbf{r}'}{pT_{k}v^{2}}, \text{ or } = 1 + \frac{a_{k}(\mathbf{r}-m\mathbf{r}')}{pv^{3}},$$

or because evidently  $\tau_k = 1$ :

$$f = \frac{T_k}{p_k} \left( \frac{dp}{dT} \right)_k = \frac{RT_k}{p_k \left( v_k - b_k \right)} - \frac{a_k \tau'_k}{p_k v^2_k}, \text{ or } = 1 + \frac{a_k \left( 1 - \tau'_k \right)}{p_k v^2_k}.$$

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After substitution of the values of s from (5),  $p_k$  from (4) and  $v_k: b_k = r$ , this becomes:

$$f = s \frac{r}{r-1} - \frac{27}{r^2} \frac{1}{\lambda_2} \tau'_k, \text{ or } = 1 + \frac{27}{r^2} \frac{1}{\lambda_2} (1 - \tau'_k), . . (6a)$$

in which also  $\frac{8}{r-1}\frac{\lambda_1}{\lambda_2}$  can be written for  $s\frac{r}{r-1}$  according to (5).

As with s = 2,77, r = 2,1 the value of  $s \frac{r}{r-1}$  or  $\frac{8}{r-1} \frac{\lambda_1}{\lambda_2}$  amounts already to 7, and also  $1 + \frac{27}{r^2} \frac{1}{\lambda_2} = 7$  — it follows necessarily that the value of  $r'_k$  must either be (almost) = 0 or exceedingly small<sup>1</sup>).

In consequence of this the  $c^{1}$  formulae (6), (7), and (8) can also be kept unchanged.

Let us now calculate the value of the characteristic function  $\varphi$ , or rather of the quantity  $\lambda = -\left(\frac{d\varphi}{dm}\right)_k$ .

Now we proved in a preceding Paper (see v. L. B, p. 1104– 1105), that when only  $\alpha$  is a function of T, the coefficients of  $\alpha^2$ and  $\beta$  in the expression (9 $\alpha$ ) for  $\lambda$  both become = 0, and that therefore only:

$$\lambda = -\frac{\varepsilon''_{t^2}}{f-1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9b)$$

is left.

In this experimentally the value -40.8 is found for  $\varepsilon''_{t^2}$ , so

<sup>1</sup>) We will just remind here of the fact, that some thirty years ago, when r was still = 3, the value -1 had to be assumed from  $f = 1 + \frac{27}{r^2}(1 - \tau'^k) = 1 + 3(1 - \tau'^k)$  for  $\tau'_k$  to make f = 7. CLAUSIUS' function  $\tau = 1 : m$  satisfied this condition, but also the better function  $\tau = e^{1-m}$  of van DER WAALS.

<sup>2</sup>) The mere fact that so high a (negative) value is found for  $\epsilon''_{t^2}$ , i.e.  $\left(\frac{d^2\epsilon}{dm^2}\right)_k$  for v constant, is a proof that  $\alpha$  (or b) must be a temperature-function. If one substitutes in the above given expression for  $F'_k$ , viz.  $F'_k = \left(\frac{d^2\epsilon_{coe^{\chi}}}{dm^2}\right) = \epsilon''_{t^2} - (\alpha^2 - \beta) \epsilon''_{v,t} - \frac{1}{6}\alpha^2 \epsilon''_{v^2,t}$ , for  $F'_k$ ,  $\epsilon''_{v,t}$  and  $\epsilon''_{v^2,t}$  resp. the values 39,6, -11.4 and 29,6 experimentally found (loc. cit. p. 1101-1103), one finds namely with  $\alpha^2 = 15$ ,  $\beta = 0.9$  for  $\epsilon''_{t^2}$  the value  $39.6 + 14.1 \cdot (-11.4) + 2.5 \cdot 29.6 = 39.6 - 160.7 + 74.0 = -47$ . If the values -11.4 and 29,6 are raised resp. to -12 and 36 for the reasons given on p. 1103-1105, one finds for  $\epsilon''_{t^2}$  the above given value -40.8. At any rate this value differs much from 0, and  $\alpha$  (or b) is therefore certainly a temperature-function.

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that  $\lambda$  with f = 7 assumes the value 40.8:6 = 6.8. [The original equation (9) gives 39.6 for  $F'_k$  with the experimental value, and of course also  $\lambda = 13.4-6.6 = 6.8$  with  $\alpha^2 = 15.2$ ,  $\beta = 0.9$ ]. This value is in perfect agreement with the course of the value of  $\varphi$  in the immediate neighbourhood of  $T_k$  (loc. cit. p. 1100-1102), from which even a somewhat higher value would follow.

Let us now calculate the value of  $\varepsilon''_{t^2}$  on the supposition that a is a function of T. From the value found above for  $\left(\frac{dp}{dT}\right)_v$ , viz.  $\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} - \frac{a_k \tau'}{T_k v^2}$ , follows immediately  $\left(\tau'' = \frac{d^2 \tau}{dm^2} = \frac{d\tau'}{dm}\right)$ :  $\left(\frac{d^2 p}{dT^2}\right)_v = -\frac{a_k \tau''}{T_k^2 v^2}$ ,

hence

$$\varepsilon''_{t^2} = \left(\frac{d^2\varepsilon}{dm^2}\right)_k = \frac{T_k^*}{p_k} \left(\frac{d^2p}{dT^2}\right)_k = -\frac{a_k \tau''_k}{p_k v_k^2},$$

so that we find;

$$a = \frac{a_k \tau''_k}{p_k v_k^2} : \frac{a_k (1 - \tau'_k)}{v_k v_k^2} = \frac{\tau''_k}{1 - \tau'_k} \quad , \qquad . \qquad . \qquad (9c)$$

when we substitute the value found above for f-1.

Now  $\tau'_k = 0$  may be put (see above), so that with  $\lambda = 6.8$  we shall have (see also p. 1106 loc. cit.):

 $\tau''_k = 6,8.$ 

So when — as an explanation of the course of  $\varphi$  at  $T_k$ — $a = a_k \tau$  is put, in which  $\tau = f(m)$ ,  $\tau$  must satisfy the two conditions:  $\tau'_k = 0$  (±) and  $\tau''_k = 7$ .

 $\beta$ ). If **b** is supposed to be a function of the temperature, then from

$$p = \frac{RT}{v - b_k \tau} - \frac{a}{v^2} , \qquad \dots \qquad \dots \qquad (1c)$$

in which  $\tau$  is therefore both a function of v and of T, follows:

$$\left(\frac{dp}{dT}\right)_{v} = \frac{R}{v - b_{k}\tau} + \frac{RT}{\left(v - b_{k}\tau\right)^{2}} \frac{b_{k}\tau'}{T_{k}} = \frac{R}{v - b_{k}\tau} \left[1 + \frac{mb_{k}\tau'}{v - b_{k}\tau}\right],$$

when  $\tau' = \frac{d\tau}{dm}$  at v constant.

Hence:

$$f = \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = \frac{RT_k}{p_k(v_k - b_k)} \left(1 + \frac{b_k \tau'_k}{v_k - b_k}\right), \quad . \quad . \quad (6b)$$

because at  $T_k$  the value of  $\tau$  is evidently again = 1. And since -

again the factor  $RT_k: p_k(v_k - b_k) = s \frac{r}{r-1}$  yields already f = 7, now too  $\tau'_k$  must be either (about) 0<sup>1</sup>), or *exceedingly small*, so that also

in this case the formulae (6), (7), and (8) can remain intact. And as for  $\tau'_k = 0$  again formula (9b) holds, viz.  $\lambda = -\varepsilon''_{t^2} : (f-1)$ , because the coefficients of  $\alpha^2$  and  $\beta$  in (9a) will be = 0 (see above at  $\alpha$ ), we again determine only  $\varepsilon''_{t^2}$ .

We find:

$$\left(\frac{d^2p}{dT^2}\right)_v = \frac{2R}{(v-b_k\tau)^2} \frac{b_k\tau'}{T_k} + \frac{2RT}{(v-b_k\tau)^2} \left(\frac{b_k\tau'}{T_k}\right)^2 + \frac{RT}{(v-b_k\tau)^2} \frac{b_k\tau''}{T_k^2}.$$

hence, when  $\tau'_k = 0$  is put:

$$\varepsilon''_{t^2} = \frac{T_k^2}{p_k} \left( \frac{d^2 p}{dT^2} \right)_k = \frac{RT_k}{p_k (v_k - b_k)^8} b_k \tau''_k = f \cdot \frac{b_k}{v_{k^-} - b_k} \tau''_k,$$

taking the value of f into account according to (6b) — when  $\tau'_k$  is put there = 0.

So we find for  $\lambda$ :

$$\lambda = -\frac{f}{f-1} \frac{\mathbf{r}''_k}{r-1}, \quad \dots \quad , \quad \dots \quad (9d)$$

in which  $\tau'' = \frac{d^2 \tau}{dm^2}$  for v constant. We draw attention to this, that  $\lambda = \tau''_k$  was found on the assumption of  $a = a_k \tau$  (formula 9c).

Now  $f: (f-1)(r-1) = 7: 6 \times 1,11 = 1,05$ , so that we must

now get:

$$\underline{\tau''_k} = -6.8 : 1.05 = -6.5.$$

So whether one takes a as temperature function or b — in both cases one will find  $\tau'_k = 0$ , and  $\tau''_k$  not far from 7, resp. — 7.

And as to the dependence of the quantity b on v,  $b'_k$  will be at most 0,1,  $v_k b''_k$  at most -0,4 (see § 1).

By the side of  $n/v^2$  no function of  $v \, can$  occur which could account at the same time for the course of the quantity  $\varphi$  at  $T_k$ , and for the known values of the critical quantities. So not VAN DER WAALS'S factor  $(1 - 1/2x)^2$  either, in which x is a function of v(see § 3).

<sup>&</sup>lt;sup>1</sup>) It is of course impossible that  $\tau'_k$  is absolutely = 0, for then the critical temperature would have an exceptional meaning in the series of temperatures between  $T = \infty$  and T = 0, to which it cannot lay claim. For quantities which have only significance in the *heterogeneous* region, where liquid and vapour coexist, there can indeed be question of a factor 1 - m in the neighbourhood of  $T_k$ , which factor would become = 0 at  $T_k (m = 1)$  — but never for quantities as a and b, for which the critical temperature is no more than an ordinary temperature. So  $\tau'_k$  can only be exceedingly small.

These are accordingly the inevitable conclusions to which the investigation of the preceding paragraphs has led us.

5. The reduced equation of state. Already in previous papers (v. L. III, p. 568, IV, p. 719) I made use of the reduced form of the equation of state, when b = f(v) was assumed in consequence of association. VAN DER WAALS has, however, (see particularly v. d. W. II) given such a form to the reduced equation of state, that the law of corresponding states was brought forward in a new form. For this purpose it was only necessary to divide the former reduced volume (expressed in  $v_k$ ) by  $\frac{3}{r} = \sqrt{\frac{f-1}{3}}$ . (The relation  $b_k : b_0$  or  $b_g : b_0$  may be left out of consideration for the present; we shall return to it in our concluding paper).

VAN DER WAALS'S results are naturally more or less approximative: first because the factors  $\lambda_1$  and  $\lambda_2$  have been disregarded, and secondly because not  $r = v_k : b_k$ , but again  $r' = v_k : b_g$  was introduced.

There is now no longer any approximation, and we get — also by a simpler way — the results found by VAN DER WAALS, perfectly defined, when p, T and v are not expressed in the *real* critical quantities  $p_k$ ,  $T_k$ , and  $v_k$  — but in the *ideal* critical quantities, i.e. those which would hold for the ideal equation of state with a and b constant. If we call the latter quantities  $p'_k$ ,  $T'_k$ , and  $v'_k$ , then

$$RT_{k} = \frac{8}{27} \lambda_{1} \frac{a}{b_{k}} ; \quad p_{k} = \frac{1}{27} \lambda_{2} \frac{a}{b_{k}^{2}} ; \quad v_{k}^{*} = r b_{k}$$
$$RT'_{k} = \frac{8}{27} \frac{a}{b_{k}} ; \quad p'_{k} = \frac{1}{27} \frac{a}{b_{k}^{2}} ; \quad v'_{k} = 3b_{k}.$$

Then from:

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

follows the equation

$$\left(\varepsilon'p'_k+\frac{a}{n'^{*}v'_k}\right)(n'v'_k-\beta'v'_k)=m'RT'_k,$$

when  $\varepsilon'$ , n', b', and m' resp. represent  $p: p'_k$ ,  $v: v'_k$ ,  $b: v'_k$ ,  $T: T'_k$ , just as formerly  $p: p_k$ ,  $v: v_k$ ,  $b: v_k$ ,  $T: T_k$  were represented by  $\varepsilon$ , n,  $\beta$ , and m.

After substitution of the above given values of  $RT'_k$ ,  $p'_k$ , and  $v'_k$ , we get therefore as before:

$$\left(\varepsilon' \cdot \frac{1}{27} \frac{a}{b_k^2} + \frac{a}{n'^2 \cdot 9b_k^2}\right) (n' \cdot 3b_k - \beta' \cdot 3b_k) = m' \cdot \frac{8}{27} \frac{a}{b_k},$$

i.e.

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Had we expressed everything in the real  $RT_k$ ,  $p_k$  and  $v_k$ , we should have got:

$$\left(\varepsilon \lambda_2 + \frac{27:r^2}{n^2}\right)(n-\beta) = \frac{8}{r} \lambda_1 m,$$

or also:

$$\left(\varepsilon + \frac{27 : \lambda_{2}r^{2}}{n^{2}}\right)(n-\beta) = \frac{8}{r}\frac{\lambda_{1}}{\lambda_{2}}m = sm, \quad . \quad . \quad (10a)$$

in which  $\beta = b : v_k = b : rb_k$ .

Hence the new reduced quantities  $\epsilon$ , m, n, and  $\beta$  of equation (10) are to the original ones in the following simple relations:

$$\varepsilon' = \lambda_2 \varepsilon = \varepsilon \times (p_k : p'_k)$$

$$m' = \lambda_1 m = m \times (T_k : T'_k)$$

$$n' = \frac{1}{s} r.n = n \times (v_k : v'_k)$$
(11)

Substitution of (11) in (10 $\alpha$ ), of course, immediately leads to (10), and vice versa.

VAN DER WAALS has retained  $\varepsilon' = \varepsilon$ , m' = m, and therefore his new reduced equation of state will in this respect only hold by approximation, though the difference will be exceedingly slight. But as VAN DER WAALS does not put  $n' = {}^{1}/{}_{s}r \cdot n$  (or  $n' = n : {}^{3}/{}_{,}$ ), but  $n' = n : {}^{3}/{}_{,'}$ , in which r' does not represent  $v_k : b_k$ , but  $v_k : b_g$ , while  $b_g$  and  $b_k$  can differ 4 or  $5^{\circ}/{}_{\circ}$ , the difference with the reduced equation of state (10) will be much greater for the quantity  $n : {}^{3}/{}_{,'}$ , because in (10) the specific element [embodied in the quantity r( $\lambda_1$  and  $\lambda_2$  left out of consideration), which quantity r can be different for different classes of bodies] has been entirely removed.

If a and b are still functions of the temperature, the term  $3:n'^{2}$  in (10) will have evidently to be replaced by  $3f(m'):n'^{2}$ , or  $\beta'$  by  $\beta'f(m')$ .

As according to (6)  $\lambda_2(f-1): 3 = 9: r^2$ , also:

$$\frac{3}{r} = \sqrt{\lambda_2 \frac{f-1}{3}},$$

and we may also write instead of  $n' = n : {}^{\mathfrak{s}}/r :$ 

$$n'=n: \sqrt{\lambda_{g}\frac{f-1}{3}},$$

now perfectly accurate.

In a following (concluding) paper some remarks will be made about the dependence of a or b on the temperature, and some general considerations will be given about the nature of the function b = f(v).

Fontanivent sur Clarens, March 1913.

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