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Physics. — "*On the value of some differential quotients in the critical point, in connection with the coexisting phases in the neighbourhood of that point and with the form of the equation of state.*" By J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

1. In some previous papers we showed that the densities d_1 and d_2 resp. of the liquid and vapour phase in the immediate neighbourhood of the critical point are represented by the expressions [1]:

$$\left. \begin{array}{l} d_1 = 1 + a\sqrt{1-m} + \beta(1-m) + \gamma(1-m)^{3/2} + \delta(1-m)^2 + \cdots \\ d_2 = 1 - a\sqrt{1-m} + \beta(1-m) - \gamma(1-m)^{3/2} + \delta(1-m)^2 - \cdots \end{array} \right\} ,(1)$$

so that for values of $m = T : T_k$ near 1 the quantities $d_1 - 1$ and $1 - d_2$ are of the order of magnitude $\sqrt{1-m}$, and *not* of the order $\sqrt[4]{1-m}$ (van der Waals, These Proc. XIII, p. 116 and 1259) or of $\sqrt[3]{1-m}$ (Goldhammer, Z. f. phys. Chem. **71**, 577 (1910)).

In his "Thermodynamische Theorie der Capillariteit" (1893) van der Waals also gives the correct expressions (see p. 44), and finds the value 2 for a with the ideal equation of state, and the value 3,5 for real (normal) substances — quite in accordance with what we found for them (loc.cit., cf. These Proc. XIV, p. 437) where the value 3,6 is given). For Fluorbenzene a may even be put 3,9 (see further). Also Mathias (Ann. de Toulouse V) gave as *empirical* formulae the theoretically correct ones.

For substances for which the ideal equation of state would hold, we find loc. cit.

$$a = 2; \quad \beta = \frac{2}{5}; \quad \gamma = -\frac{13}{25}; \quad \delta = \frac{128}{875}; \quad \varepsilon = \frac{1359}{17500}.$$

The coefficient a indicates the *divergence* of the phases in the critical point; the coefficient β is nothing but the coefficient of direction of the so-called straight diameter $\frac{1}{2}(d_1 + d_2) = f(m)$ in that same point.

When we pass from the ideal equation of state to the real one, β increases from 0,4 to about 0,9, whereas a increases from 2 to about 3,9.

2. We shall now demonstrate that the expressions (1) will hold for any form of the possible equation of state, and that $d_1 - 1$ and $1 - d_2$ would only be of the order $\sqrt[4]{1-m}$, when in the critical point not

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[1] See among others These Proc. XIV, p. 438 et seq., 563 et seq. and 574.

only $\dfrac{dp}{dv}$ and $\dfrac{d^2p}{dv^2}$ are equal to 0, but also $\dfrac{d^3p}{dv^3}$ and $\dfrac{d^4p}{dv^4}$. And as the latter is evidently an impossibility (for then there would be *relations* between the coefficients of the equation of state), $d_1 - 1$ can never be of the order of magnitude $\sqrt[\nu]{1-m}$ either. Other exponents, like $\sqrt[\nu]{1-m}$, are of course quite excluded.

For if we put quite generally

$$p = f(v, T),$$

we have, when ε, n, and m represent resp. "reduced" 'pressure, volume and temperature, in the neighbourhood of the critical point :

$$\varepsilon = 1 + \left[\varepsilon'_v (n-1) + \varepsilon'_t (m-1) \right] + \left[\frac{1}{2} \varepsilon''_{v^2}(n-1)^2 + \varepsilon''_{v,t}(n-1)(m-1) + \right.$$
$$\left. + \frac{1}{2} \varepsilon''_{t^2}(m-1)^2 \right] + \left[\frac{1}{6} \varepsilon'''_{v^3}(n-1)^3 + \text{etc.} \right] + \text{etc.}$$

In this ε'_v represents $\left(\dfrac{\partial \varepsilon}{\partial n}\right)_{kr}$; ε'_t represents $\left(\dfrac{\partial \varepsilon}{\partial m}\right)_{kr}$; ε''_{v^2} represents $\left(\dfrac{\partial^2 \varepsilon}{\partial n^2}\right)_{kr}$; etc.

The determination of the coefficient a will require no other differential quotients than the above mentioned ones. In this ε'_v and ε''_{v^2} are both $= 0$ at the critical point, so that by equation of the values of ε in the two coexisting phases

$$\varepsilon''_{v,t}(m-1)\left[(n_2-1)-(n_1-1)\right] + \frac{1}{6}\varepsilon'''_{v^3}\left[(n_2-1)^3-(n_1-1)^3\right] + .. = 0$$

remains, because also the terms with only $m-1$ and $(m-1)^2$ vanish in consequence of the equality of the temperature.

If we now put :

$$n_2 = 1 + a\tau + \beta'\tau^2 + ..; \quad n_1 = 1 - a\tau + \beta'\tau^2 + ...,$$

in which τ represents a power of $1-m$ *as yet unknown*, we get

$$n_2 - 1 = a\tau + \beta'\tau^2 ... = \theta_2; \quad n_1 - 1 = -(a\tau - \beta'\tau^2 ..) = -\theta_1,$$

and hence :

$$\varepsilon''_{v,t}(m-1)(\theta_2+\theta_1) + \frac{1}{6}\varepsilon'''_{v^3}(\theta^3_2+\theta^3_1) + ... = 0,$$

or

$$\varepsilon''_{v,t}(1-m) = \frac{1}{6}\varepsilon'''_{v^3}\frac{\theta^3_2+\theta^3_1}{\theta_2+\theta_1} + ...$$

Now evidently (the higher powers we shall want presently) :

$$\theta_2 + \theta_1 = 2a\tau..; \qquad \theta^2_2 - \theta^2_1 = 4a\beta'\tau^3..; \qquad \theta^3_2 + \theta^3_1 = 2a^3\tau^3..$$
$$\theta^3_2 - \theta^3_1 = 6a^2\beta'\tau^4..; \quad \theta^4_2 - \theta^4_1 = 8a^3\beta'\tau^5..; \quad \theta^5_2 + \theta^5_1 = 2a^5\tau^5..$$

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so that

$$\frac{\theta^3_2 + \theta^3_1}{\theta_2 + \theta_1} = a^2\tau^2 \; ..$$

Hence we get:

$$\varepsilon''_{v,t}(1-m) = \frac{1}{6}\varepsilon'''_{v^3}(a^2\tau^2 \; ..) + \; .., \quad . \quad . \quad . \quad . \quad . \quad (a)$$

so that it now appears with the utmost clearness that τ^2 must be of the order $1-m$, and so τ of the order $\sqrt{1-m}$.

Even if n_2 were $= 1 + a\tau ..$, $n_1 = 1 - a'\tau ..$, in which a' is $not = a$ (which, however, is impossible: see also These Proc. XIV, p .439 and 440), even then τ would appear to be of the order $\sqrt{1-m}$ according to the above. For then $\theta_2 + \theta_1$ would be $= (a + a')\tau ..$, $\theta^3_2 + \theta^3_1 = $ $= (a^3 + a'^3)\tau^3 ..$, and hence $\dfrac{\theta^3_2 + \theta^3_1}{\theta_2 + \theta_1} = (a^2 - aa' + a'^2)\tau^2$, so that the conclusion would remain the same.

Only when also ε'''_{v^3}, i. e. $\left(\dfrac{\partial^3 \varepsilon}{\partial n^3}\right)_{kr}$ were $= 0$ — but then ε''''_{v^4} would also have to be $= 0$ on account of the form of the critical isotherm (which of course runs from $p = \infty$ to $p = 0$) — only then we should have:

$$\varepsilon''_{v,t}(m-1)(\theta_2 + \theta_1) + \frac{1}{6}\left[3\varepsilon'''_{v^2,t}(m-1)(\theta^2_2 - \theta^2_1) + \; ..\right] +$$

$$+ \frac{1}{24}\left[4\varepsilon''''_{v^3,t}(m-1)(\theta^3_2 + \theta^3_1) + \; ..\right] + \frac{1}{120}\varepsilon^V_{v^5}(\theta^5_2 + \theta^5_1) + \text{etc.} = 0.$$

But from this would follow:

$$(m-1)\left[\varepsilon''_{v,t} \cdot 2a\tau ..\right] + \; .. + \frac{1}{120}\varepsilon^V_{v^5}(2a^5\tau^5 ..) + \; .. = 0.$$

and so $1-m$ would be of the order τ^4, i. e. τ of the order $\sqrt{1-m}$. So for this the (impossible) supposition ε'''_{v^3} and $\varepsilon''''_{v^4} = 0$ would be required [1].

3. Let us proceed after these considerations to the expressions for the coefficients a and β'.

As now henceforth τ^2 can be replaced by $1-m$, (a) passes into

$$\varepsilon''_{v,t} = \frac{1}{6}\varepsilon'''_{v^3}a^2,$$

after equation of the coefficients of the different powers of $1-m$;

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[1] If only $\varepsilon'''_{v^3} = 0$, we should have got $\dfrac{1}{24}\varepsilon''''_{v^4}(\theta^4_2 - \theta^4_1)$ instead of $\dfrac{1}{120}\varepsilon^V_{v^5}(2a^5\tau^5 ..)$, hence as $\theta^4_2 - \theta^4_1 = 8a^3\beta'\tau^5$, $1-m$ is again of the order τ^4.

from which follows:

$$a^2 = \frac{6\varepsilon''_{v,t}}{\varepsilon'''_{v^3}}, \qquad \qquad \qquad (1)$$

being the quite general formula for the coefficient a, whatever may be the form of the equation of state $\varepsilon = f(m,n)$ [1].

What follows may serve as a control. The ideal equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{or} \quad \varepsilon = \frac{8m}{3n-1} - \frac{3}{n^2}$$

gives for the different differentialquotients:

$$\frac{\partial \varepsilon}{\partial n} = -\frac{24m}{(3n-1)^2} + \frac{6}{n^3} \left| \frac{\partial^2 \varepsilon}{\partial n^2} = \frac{144m}{(3n-1)^3} - \frac{18}{n^4} \right| \frac{\partial^3 \varepsilon}{\partial n^3} = -\frac{9 \times 144m}{(3n-1)^4} + \frac{72}{n^5}$$

$$\frac{\partial^4 \varepsilon}{\partial n^4} = \frac{9 \times 12 \times 144m}{(3n-1)^5} - \frac{360}{n^6} \left| \frac{\partial^2 \varepsilon}{\partial n \partial m} = -\frac{24}{(3n-1)^2} \right| \frac{\partial^3 \varepsilon}{\partial n^2 \partial m} = \frac{144}{(3n-1)^3}.$$

So this becomes for T_k :

$$\varepsilon'_v = -6 + 6 = 0 \mid \varepsilon''_{v^2} = 18 - 18 = 0 \mid \varepsilon'''_{v^3} = -81 + 72 = -9$$

$$\varepsilon''''_{v^4} = 486 - 360 = 126 \mid \varepsilon''_{v,t} = -6 \mid \varepsilon'''_{v^2,t} = 18.$$

Thus we find for a^2 according to (1):

$$a^2 = \frac{6 \times -6}{-9} = 4,$$

hence $a = 2$, as it should be.

If in (α) we also take the terms with τ^4 into account, we get an equation between the coefficients α, β', and γ'. So we cannot determine β' from this. For this we shall have to find the relation of coexistence between the two phases. This is found from (ε_c denotes the pressure of coexistence)

$$\varepsilon_c = \frac{1}{n_2 - n_1} \int_{n_1-1}^{n_2-1} \varepsilon \, . \, d\,(n-1).$$

With

$$\varepsilon = 1 + \varepsilon'_t(m-1) + \left[\varepsilon''_{v,t}(n-1)(m-1) + \frac{1}{2}\varepsilon''_{t^2}(m-1)^2 \right] + \\ + \left[\frac{1}{6}\varepsilon'''_{v^3}(n-1)^3 + \frac{1}{2}\varepsilon'''_{v^2,t}(n-1)^2(m-1) + \frac{1}{2}\varepsilon'''_{v,t^2}(n-1)(m-1)^2 + \right. \\ \left. + \frac{1}{6}\varepsilon'''_{t^3}(m-1)^3 \right] + \frac{1}{24}\varepsilon''''_{v^4}(n-1)^4 + \dots \bigg\}(\alpha)$$

this becomes:

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[1] Cf v. d. WAALS, Capillariteit, p. 44.

$$\varepsilon_c = 1 + \varepsilon'_t(m-1) + \left[\frac{1}{2}\varepsilon''_{v,t}\frac{\theta^2_2-\theta^2_1}{\theta_2+\theta_1}(m-1) + \frac{1}{2}\varepsilon''_{t^2}(m-1)^2\right] + $$

$$+ \left[\frac{1}{24}\varepsilon'''_{v^3}\frac{\theta^4_2-\theta^4_1}{\theta_2+\theta_1} + \frac{1}{6}\varepsilon'''_{v^2,t}\frac{\theta^3_2+\theta^3_1}{\theta_2+\theta_1}(m-1) + \frac{1}{4}\varepsilon'''_{v,t^2}\frac{\theta^2_2-\theta^2_1}{\theta_2+\theta_1}(m-1)^2 + \right. $$

$$\left. + \frac{1}{6}\varepsilon'''_{t^3}(m-1)^3\right] + \frac{1}{120}\varepsilon''''_{v^4}\frac{\theta^5_2+\theta^5_1}{\theta_2+\theta_1} + \cdot \cdot \quad\Bigg\}\,,(b)$$

as $(n_2-1) - (n_1-1) = \theta_2 + \theta_1$, $(n_2-1)^2 - (n_1-1)^2 = \theta^2_2-\theta^2_1$, etc. (see above).

If in (α) we substitute successively n_2 and n_1 for n, and then take half the sum, we get:

$$\varepsilon = 1 + \varepsilon'_t(m-1) + \left[\varepsilon''_{v,t}\frac{\theta_2-\theta_1}{2}(m-1) + \frac{1}{2}\varepsilon''_{t^2}(m-1)^2\right] +$$

$$+ \left[\frac{1}{6}\varepsilon'''_{v^3}\frac{\theta^3_2-\theta^3_1}{2} + \frac{1}{2}\varepsilon'''_{v^2,t}\frac{\theta^2_2+\theta^2_1}{2}(m-1) + \frac{1}{2}\varepsilon'''_{v,t^2}\frac{\theta_2-\theta_1}{2}(m-1)^2 + \right.$$

$$\left. + \frac{1}{6}\varepsilon'''_{v^3}(m-1)^3\right] + \frac{1}{24}\varepsilon''''_{v^4}\frac{\theta^4_2+\theta^4_1}{2} + \cdot \cdot \quad\Bigg\}\,,(a')$$

Equation of (b) and (a') now yields with $1 - m = -(m-1) = \tau^2$:

$$- \varepsilon''_{v,t}\left[\frac{1}{2}\frac{\theta^2_2-\theta^2_1}{\theta_2+\theta_1} - \frac{\theta_2-\theta_1}{2}\right] + \frac{1}{6}\varepsilon'''_{v^3}\left[\frac{1}{4}\frac{\theta^4_2-\theta^4_1}{\theta_2+\theta_1} - \frac{\theta^3_2-\theta^3_1}{2}\right] -$$

$$- \frac{1}{2}\varepsilon'''_{v^2,t}\tau^2\left[\frac{1}{3}\frac{\theta^3_2+\theta^3_1}{\theta_2+\theta_1} - \frac{\theta^2_2+\theta^2_1}{2}\right] + \frac{1}{2}\varepsilon'''_{v,t^2}\tau^1\left[\frac{1}{2}\frac{\theta^2_2-\theta^2_1}{\theta_2+\theta_1} - \frac{\theta_2-\theta_1}{2}\right] +$$

$$+ \frac{1}{24}\varepsilon''''_{v^4}\left[\frac{1}{5}\frac{\theta^5_2+\theta^5_1}{\theta_2+\theta_1} - \frac{\theta^4_2+\theta^4_1}{2}\right] + \cdot \cdot = 0.$$

With the values of $\theta_2 + \theta_1$, $\theta^2_2 - \theta^2_1$, etc. given above in § 2 this becomes (the coefficients of $\varepsilon''_{v,t}$ and ε'''_{v,t^2} are evidently $= 0$):

$$\frac{1}{6}\varepsilon'''_{v^3}\left[\alpha^2\beta'\tau^4 - 3\,\alpha^2\beta'\tau^4 \cdot \cdot\right] - \frac{1}{2}\varepsilon'''_{v^2,t}\tau^2\left[\frac{1}{3}\alpha^2\tau^2 - \alpha^2\tau^2 \cdot \cdot\right] +$$

$$+ \frac{1}{24}\varepsilon''''_{v^4}\left[\frac{1}{5}\alpha^4\tau^4 - \alpha^4\tau^4\right] = 0,$$

because evidently $(\theta^4_2 + \theta^4_1) : 2 = \alpha^4\tau^4$. In this way we only get the terms with τ^4, and find:

$$- \frac{1}{3}\varepsilon'''_{v^3}\alpha^2\beta' + \frac{1}{3}\varepsilon'''_{v^2,t}\alpha^2 - \frac{1}{30}\varepsilon''''_{v^4}\alpha^4 = 0,$$

hence finally:

$$\beta' = \frac{\varepsilon''_{v^2,t} - \dfrac{1}{10}\, a^2 \varepsilon''''_{v^t}}{\varepsilon'''_{v^3}}, \qquad \ldots \ldots \ldots \quad (2)$$

in which a^2 is given by (1).

So the expression derived by VAN DER WAALS (Capillariteit, p. 44), viz. $\beta' = \varepsilon'''_{v^2,t} : \varepsilon'''_{v^3}$, is inaccurate on account of the neglect of the term with ε''''_{v^t}. Besides, the control by means of the ideal equation of state confirms this. As we put $n_2 = 1 + a\tau + \beta'\tau^2 \ldots,\ d_2 = = 1 - a\tau + \beta\tau^2 \ldots$, evidently

$$\beta = a^2 - \beta',$$

because $d_2 = 1 : n_2$.

Now by means of the above given values of the differential-quotients $(a^2 = 4)$ we find from (2):

$$\beta' = \frac{18 - \dfrac{2}{5}\cdot 126}{-9} = -2 + \frac{28}{5} = 3\,\frac{3}{5},$$

giving $\beta = 4 - 3\,\dfrac{3}{5} = \dfrac{2}{5}$, in accordance with what we found before (see § 1).

VAN DER WAALS's expression would have given an entirely erroneous value for β.

4. *The value of the characteristic function.*
If we put

$$\frac{m}{\varepsilon}\frac{d\varepsilon_c}{dm} = f,$$

we shall understand by the "characteristic function" φ the value of:

$$\varphi = \frac{f-1}{f_k-1}\cdot\frac{\varepsilon}{d_1 d_2},$$

of which we know that it is equal to 1, when the quantities a and b of the equation of state do *not* depend on the temperature T (or a only linearly on T). But in any other case φ will no longer be $= 1$, but it will be represented in the neighbourhood of the critical point by

$$\varphi = 1 + \lambda\,(1 - m),$$

in which we shall determine the coefficient λ.

In our previous paper (These Proc. XIV, p. 777) we have viz. already shown, that when the said suppositions are fulfilled, formula (8) given there holds, viz.

$$\frac{T}{p}\frac{dp_c}{dT} = 1 + \frac{a}{pv_1v_2},$$

i. e.

$$f = \frac{m}{\varepsilon}\frac{d\varepsilon_c}{dm} = 1 + \frac{a}{p_kv_k^2}\cdot\frac{d_1d_2}{\varepsilon},$$

when ε_c denotes the pressure of coexistence, through which we distinguish $\frac{d\varepsilon_c}{dm}$ from $\left(\frac{\partial m}{\partial\varepsilon}\right)_n$. So we have also:

$$f_k = 1 + \frac{a}{p_kv_k^2},$$

hence

$$\frac{f-1}{f_k-1} = \frac{d_1d_2}{\varepsilon},$$

in other words $\varphi = 1$.

If, however, a and b are also functions of the temperature, we have generally according to (b) of § 3, taking the values of $\theta_2+\theta_1$, etc. into account, and disregarding all the powers of $m-1$ higher than the second:

$$\varepsilon_c = 1 + \varepsilon'_t(m-1) + \left[\frac{1}{2}\varepsilon''_{v,t}\cdot 2\beta'\tau^2(m-1) + \frac{1}{2}\varepsilon''_{t^2}(m-1)^2\right] +$$

$$+ \left[\frac{1}{24}\varepsilon'''_{v^3}\cdot 4\alpha^2\beta'\tau^4 + \frac{1}{6}\varepsilon'''_{v^2,t}\cdot\alpha^2\tau^2(m-1)..\right] + \frac{1}{120}\varepsilon''''_{v^4}\cdot\alpha^4\tau^4,$$

or as $\tau^2 = 1-m = -(m-1)$:

$$\varepsilon_c = 1 + \varepsilon'_t(m-1) + \left[-\varepsilon''_{v,t}\beta'(m-1)^2 + \frac{1}{2}\varepsilon''_{t^2}(m-1)^2\right] +$$

$$+ \left[\frac{1}{6}\varepsilon'''_{v^3}\alpha^2\beta'(m-1)^2 - \frac{1}{6}\varepsilon'''_{v^2,t}\alpha^2(m-1)^2.\right] + \frac{1}{120}\varepsilon''''_{v^4}\alpha^4(m-1)^2.$$

From this follows:

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t + \left[2\varepsilon''_{v,t}\beta'(1-m) - \varepsilon''_{t^2}(1-m)\right] +$$

$$+ \left[-\frac{1}{3}\varepsilon'''_{v^3}\alpha^2\beta'(1-m) + \frac{1}{3}\varepsilon'''_{v^2,t}\alpha^2(1-m)\right] - \frac{1}{60}\varepsilon''''_{v^4}\alpha^4(1-m),$$

i. e.

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m)\left[\varepsilon''_{t^2} - 2\varepsilon''_{v,t}\beta' + \frac{1}{3}\varepsilon'''_{v^3}\alpha^2\beta' - \frac{1}{3}\varepsilon'''_{v^2,t}\alpha^2 + \frac{1}{60}\varepsilon''''_{v^4}\alpha^4\right].$$

In this $-2\varepsilon''_{v,t}\beta' + \frac{1}{3}\varepsilon'''_{v^3}\alpha^2\beta' = 0$ according to the formula (1) for α^2 derived above, so that we keep:

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$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m)\left[\varepsilon''_{t^2} - \frac{1}{3}\,a^2\left(\varepsilon'''_{v^2,t} - \frac{1}{20}\,a^2\,\varepsilon''''_{v^4}\right)\right].$$

Further according to formula (2) we have:

$$-\frac{1}{20}\,a^2\,\varepsilon''''_{v^4} = \frac{1}{2}\,\varepsilon'''_{v^3}\,\beta' - \frac{1}{2}\,\varepsilon'''_{v^2,t},$$

so that we get:

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m)\left[\varepsilon''_{t^2} - \frac{1}{6}\,a^2\left(\varepsilon'''_{v^3}\,\beta' + \varepsilon''_{v^2,t}\right)\right],$$

or as $a^2\,\varepsilon'''_{v^3} = 6\,\varepsilon''_{v,t}$ according to (1), also

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m)\left[\varepsilon''_{t^2} - \beta'\,\varepsilon''_{v,t} - \frac{1}{6}\,a^2\,\varepsilon'''_{v^2,t}\right] = \varepsilon'_t - \omega(1-m), \qquad . \quad (3)$$

in which $\varepsilon'_t = \left(\dfrac{\partial\varepsilon}{\partial m}\right)_{kr.}$ $\Big[$ With the ideal equation of state, where

(see above) $\varepsilon''_{t^2} = 0$, $\varepsilon''_{r,t} = -6$, $\varepsilon'''_{v^2,t} = 18$, ω becomes $=$

$$= 0 - \frac{18}{5}\,(-6) - \frac{1}{6}\cdot 4 \cdot 18 = \frac{108}{5} - 12 = 9\frac{3}{5}\Big].$$

So for $f_k = \left(\dfrac{m\,d\varepsilon_c}{\varepsilon\,dm}\right)_{kr.} = \left(\dfrac{d\varepsilon_c}{dm}\right)_{kr.} = \varepsilon'$ we find properly:

$$f_k = \varepsilon' = \varepsilon'_t.$$

The value of this is $= \dfrac{8}{3n_k - 1} = 4$ for the ideal equation of

state, and becomes $= 7$ for all ordinary normal substances.

As $m = 1 - (1-m)$ and $\varepsilon = 1 - \varepsilon'(1-m)$, we now get for φ:

$$\varphi = \frac{\dfrac{1 - (1-m)}{1 - \varepsilon'_t(1-m)}\left[\varepsilon'_t - \omega(1-m)\right] - 1}{\varepsilon'_t - 1} \times \frac{1 - \varepsilon'_t(1-m)}{1 - (a^2 - 2\beta)(1-m)},$$

seeing that $d_1\,d_2 = [1 + a\sqrt{1-m} + \beta(1-m)]\,[1 - a\sqrt{1-m} + \beta(1-m)] = 1 - (a^2 - 2\beta)(1-m)$.

After some reduction this becomes:

$$\varphi = \frac{\varepsilon'_t - \omega(1-m) - 1}{\varepsilon'_t - 1} \times \frac{1}{1 - (a^2 - 2\beta)(1-m)},$$

or

$$\varphi = \frac{1 - \dfrac{\omega}{\varepsilon'_t - 1}(1-m)}{1 - (a^2 - 2\beta)(1-m)} = 1 + \lambda(1-m). \qquad . \quad (4)$$

As now $\lambda = 0$ with the ideal equation of state, i.e. with that in which a and b are no functions of T (or a only depends linearly on T), in this limiting case must hold:

$$\frac{\omega}{\varepsilon'_t - 1} = \alpha^2 - 2\beta.$$

But as ω is evidently $= \left(\dfrac{d^2\varepsilon_c}{dm^2}\right)_{kr} = f'_k$, we may also write for this:

$$\frac{f'_k}{f_k - 1} = \alpha^2 - 2\beta,$$

which relation was derived in my preceding communication (These Proc. XIV, p. 779). But in all other cases λ is not equal to 0, and we have :

$$\lambda = (\alpha^2 - 2\beta) - \frac{f'_k}{f_k - 1} \quad \cdots \cdots \cdots \quad (5)$$

From (4) we see also that φ *cannot* be $= 1 + \sqrt{1 - m} \; - \; ^1/_2$ $(1 - m)$, i.e. of the order $\sqrt{1 - m}$ near T_k, but must be of the order $1 - m$. I pointed this already out in my preceding communication (loc. cit. p. 778, footnote). So though the empirical formula for φ drawn up by v. D. WAALS very well renders the values following from YOUNG's tables — theoretically it cannot be upheld.

5. After the above derivations we may proceed to determine the values of some differential quotients for a normal substance as e.g. Fluorbenzene. From YOUNG's tables (Dublin Soc. June 1910), the following values of m, ε, d_1, d_2, $^1/_2 (d_1 + d_2)$, $^1/_2 (d_1 - d_2)$ and φ have been calculated. (See p. 1100).

For T_k has been found $286°,55$; for p_k YOUNG gives 33912 mm. of mercury; for d_k the value $0,3541$ has been assumed. The values of F are those which can be calculated from the vapour pressure formula

$$- \log \varepsilon_c = F \frac{1 - m}{m}.$$

The values of $f = \dfrac{\varepsilon}{m}\dfrac{d\varepsilon_c}{dm}$ have been calculated as follows. From the above formula follows :

$$- \frac{1}{\varepsilon}\frac{d\varepsilon_c}{dm} = - \frac{F}{m^2} + \frac{1 - m}{m}\frac{dF}{dm},$$

so that we get :

$$f = \frac{m}{\varepsilon}\frac{d\varepsilon_c}{dm} = \frac{F}{m} - (1 - m)\frac{dF}{dm}.$$

A minimum $(F = 6,67)$ is observed in the values of F at $m = 0,77$. If we had continued the table up to $m = 0,45$, F would already have increased again to $7,11$. The value of φ at first rapidly in-

m	ε	d_1	d_2	$\frac{1}{2}(d_1+d_2)$	$\frac{1}{2}(d_1-d_2)$	F	$f=\frac{m}{\varepsilon}\frac{d^2\varepsilon}{dm}$	φ
0.6309	0.01902	2.682	0.008144	1.345	1.337	6.773	10.80	1.41
0.6488	0.02604	2.645	0.01086	1.328	1.317	6.740	10.44	1.41
0.6667	0.03471	2.607	0 01422	1.311	1.296	6.723	10.11	1.41
0.6845	0.04547	2.569	0.01844	1.294	1.275	6.706	9.822	1.40
0.7024	0.05865	2.529	0.02357	1.276	1.253	6.694	9.547	1.39
0.7203	0.07460	2.488	0.02974	1.259	1.229	6.685	9.293	1.38
0.7381	0.09354	2.447	0.03716	1.242	1.205	6.678	9.053	1.37
0.7560	0.1159	2.406	0.04600	1.226	1.180	6.678	8.837	1.35
0.7739	0.1424	2.362	0.05625	1.209	1.153	6.672*	8.617	1.35
0.7917	0.1722	2.317	0.06814	1.193	1.124	6.685	8.425	1.34
0.8096	0.2066	2.270	0.08221	1.176	1.094	6.705	8.270	1.33
0.8275	0.2470	2.219	0.09873	1.159	1.060	6.708	8.095	1.32
0.8453	0.2919	2 166	0.1182	1.142	1.024	6.728	7.937	1.30
0.8632	0.3426	2.112	0.1403	1.126	0.986	6.759	7.804	1.30
0.8811	0.3996	2.052	0.1668	1.109	0.943	6.797	7.690	1.29
0.8989	0.4637	1.987	0.1987	1.093	0.894	6.833	7.579	1.28
0.9168	0.5355	1.917	0.2373	1.077	0.840	6.882	7.487	1.26
0.9347	0.6165	1.837	0.2847	1.061	0.776	6.921	7.388	1.24 .
0.9525	0.7065	1.740	0.3463	1.043	0.697	6.972	7.305	1.22
0.9704	0.8069	1.621	0.4335	1.027	0.594	7.036	7.250	1.18
0.9883	0.9205	1.450	0.5744	1.012	0.438	6.984	7.071	1.11
1.0000	1.0000	1.000	1.0000	1.000	0.000	—	—	1.00

creases from $m=1$, but then more slowly, and it seems to approach asymptotically to about 1,5. Its course is very well represented by VAN DER WAALS's formula, but as we already stated, near T_k $\varphi-1$ is not of the order $\sqrt{1-m}$, but of the order $1-m$.

How closely the empirical formula $\varphi=1+\sqrt{1-m}-\frac{1}{2}(1-m)$ renders the course, may appear from the following table, p. 1101.

Whereas the agreement between the calculated and the found values of $\varphi-1$ at $m=0,70$ and $0,86$ is perfect, the discrepancies at $m=0,97$ and $0,99$ amount to about 10%.

From the values of m and ε occurring in the table, we can now

m	r	Found
0	$1 + 1 \quad -0.50 = 1.50$	—
0.7024	$1 + 0.543 - 0.149 = 1.394$	1.39
0.8632	$1 + 0.370 - 0.068 = 1.302$	1.30
0.9704	$1 + 0.172 - 0.015 = 1.157$	1.18
0.9883	$1 + 0.108 - 0.006 = 1.102$	1.11

easily calculate, making use of the six values of m from 0,8632 to 0,9525 (the last included):

$$\varepsilon_c = 1 - 7,065 (1 - m) + 19.8 (1 - m)^2 - 24,0 (1 - m)^3,$$

so that we have:

$$f_k = \varepsilon' = \varepsilon'_t = 7,065 \mid f''_k = \varepsilon'' \left(= \left(\frac{d^2 \varepsilon_c}{dm^2} \right)_{kr} = \omega \right) = 39,6.$$

So 6,6 is found for $\dfrac{f'_k}{f_k - 1}$. $\left[\text{With the ideal equation of state this} \right.$

value is $= \dfrac{9,6}{4-1} = 3,2 \Big]$.

Let us now determine the values of the coefficients a and β in the expansions into series for d_1 and d_2.

With $\frac{1}{2} (d_1 + d_2) = \beta (1 - m) + \delta (1 - m)^2$ we calculate from the table for $m = 0,8632$ etc. the following values

$$\beta = 0,913 \mid \delta = 0.055.$$

And from $\frac{1}{2} (d_1 - d_2) \sqrt{ = a} + 1 - m \, \gamma (1 - m) + \varepsilon (1 - m)^2$ we can calculate:

$$a = 3,9 \mid \gamma = -15,3 \mid \varepsilon = 48.$$

Now the value of $\beta' = a^2 - \beta$ (β' is the coefficient of $1 - m$ in $n_2 = 1 + a \sqrt{1 - m} + \beta' (1 - m) + \ldots$, see above) becomes:

$$\beta' = 15,2 - 0,9 = 14,3,$$

which for the ideal equation of state $= 4 - 0,4 = 3,6$, so exactly the fourth part.

And for $a^2 - 2\beta$ we find $15,2 - 1,8 = 13,4$. [With the ideal equation of state $4 - 2 \times 0,4 = 3,2$ is found for the value of $a^2 - 2\beta$].

For λ we find now according to (5):

$$\lambda = 13,4 - 6,6 = 6,8,$$

so that according to (4) close to T_c:

$$\varphi = 1 + 6,8 (1 - m).$$

So for $m = 0,9883$ q would be $= 1 + 6,8 \times 0,0117 = 1,08$, and for $m = 0,9704$ q would be $= 1 + 6,8 \times 0,0296 = 1,20$ (found 1,11 1,18). So $\lambda = 6,8$ is possibly still somewhat too low, but it is also possible — and this I think more likely — that the values of d_1 and d_2, found experimentally near the critical point, are not quite accurate, in consequence of which φ is found too high. So most likely the value of the product $d_1 d_2$ is too low, on account of the density of the liquid phase being measured too small in consequence of imperfect homogeneity (presence of vapour bubbles), or because the thickness of the capillary layer, which is of measurable dimensions at the critical point, has not been taken into account, in which layer the density is of course smaller than in the *homogeneous* liquid phase.

In consequence of this the locus $\frac{1}{2}(d_1 + d_2) = f(m)$ deviates seemingly too much to the liquid side quite near the critical point, and accordingly the abrupt deflection of this locus close to T_c, found by YOUNG, CARDOSO and others, would disappear, when the density of the liquid phase could be measured more accurately.

6. The value of the differentialquotients $\varepsilon''_{v,t} = \left(\dfrac{\partial^2 \varepsilon}{\partial n \partial m}\right)_{kr}$ and $\varepsilon'''_{v^2 t} = \left(\dfrac{\partial^3 \varepsilon}{\partial n^2 \partial m}\right)_{kr}$ may be calculated from data of isotherms quite near the critical temperature. Those for $C_6 H_5 F$ not being at my disposal, I could only make use of DORSMAN's data (Thesis for the Doctorate) for CO_2. For $33°.1$ he finds e. g. $p = 75,30$, $76,10$, $77,75$ resp. for $v = 551$, 449 and 343. From this we can calculate that $\dfrac{dp}{dv}$ for $v = 438$ (the volume on the isotherm of $33°,1$ that agrees with the critical volume) has the value $-0,01245$. From this the value $\dfrac{438}{73} \times -0,01245 = -0,0747$ follows for $\left(\dfrac{\partial \varepsilon}{\partial n}\right)_{33,1}$ (the critical pressure is viz. $= 73$).

So we have $(31°,1$ is the critical temperature):

$$\left(\frac{\partial \varepsilon}{\partial n}\right)_{31,1} = 0 \quad ; \quad \left(\frac{\partial \varepsilon}{\partial n}\right)_{33,1} = -0,0747 \text{ (both for } v = v_k).$$

Hence (the absolute temperature at $t = 32°,1$ is $305,2$)

$$\varepsilon''_{v,t} = \left(\frac{\partial^2 \varepsilon}{\partial n \partial m}\right)_{kr} = -\frac{0,0747}{2} \times 305,2 = -11,4.$$

We saw above that the ideal equation of state gives for this -6. From the same data the value $0,00007432$ can be derived for

$\dfrac{d^2p}{dv^2}$ at $v = 438$ and $33°.1$ [The data can viz. be rendered by the formula $p = 76,10 - 0,01163\,(v - 449) + + 0,00003716\,(v - 449)^2$, from which easily $\dfrac{dv}{dp}$ and $\dfrac{d^2p}{dv^2}$ for $v = 438$ can be derived].

So for $\dfrac{\partial^2\varepsilon}{\partial n^2}$ we find $\dfrac{(433)^2}{73} \times 0,00007432 = 0,1953$. Hence we have:

$$\left(\frac{\partial^2\varepsilon}{\partial n^2}\right)_{31,1} = 0 \quad ; \quad \left(\frac{\partial^2\varepsilon}{\partial n^2}\right)_{33,1} = 0,1953 \quad \text{(both for } v = v_k\text{)},$$

and from this follows:

$$\varepsilon'''_{v^2,t} = \left(\frac{\partial^3\varepsilon}{\partial n^2\partial m}\right)_{kr} = \frac{0,1953}{2} \times 305,2 = 29,8.$$

For the ideal equation of state we find 18 for this.

Now in virtue of considerations which will presently be explained, we shall raise the values $-11,4$ and $29,8$ to -12 and 36, as these values cannot differ much from *double* the values in case the ideal equation of state is used. It follows also from the nature of the above indicated calculation, that the found values $-11,4$ and $29,8$ cannot lay claim to very great accuracy.

Now we can also find the values of ε'''_{v^3} and ε'''_{v^t}. From (1) follows viz.:

$$\varepsilon'''_{v^3} = \frac{6\varepsilon''_{v,t}}{a^2} = \frac{6 \times (-12)}{15.2} = -4,7.$$

The ideal equation of state gives about double the value, viz.— 9. We find further from (2):

$$\frac{1}{10}\,a^2\varepsilon'''_{v^4} = \varepsilon'''_{v^2,t} - \beta'\varepsilon'''_{v^3} = 36 - 14,3 \times (-4,7) = 103,2,$$

hence

$$\varepsilon''_{v^t} = 103,2 : 1,52 = 67,9,$$

for which with the ideal equation of state also about double the value is found, viz. 126.

Finally we can calculate $\varepsilon''_{t^2} = \left(\dfrac{\partial^2\varepsilon}{\partial m^2}\right)_{kr}$ from $\varepsilon'' = \omega = 39,6$, in which ω is represented according to (3) by

$$\omega = \varepsilon''_{t^2} - \beta'\varepsilon''_{v,t} - {}^1/_6\,a^2\varepsilon'''_{v^2,t}.$$

So we find:

$$\varepsilon''_{t^2} = 39,6 + 14,3 \times (-12) + {}^1/_6 \times 15,2 \times 36,$$

or

$$\varepsilon''_{t^2} = 39,6 - 171,6 + 91,2 = -40,8.$$

The value of this differentialquotient is $= 0$ with the ideal equation of state. The great negative value of ε''_{t^2} for real substances points — as we shall presently see — to a great positive value of $\dfrac{d^2 a}{dt^2}$.

We have now the following survey (all this at T_k).

v	β	$\beta'=v^2-\varepsilon$	$\varepsilon'_t=\varepsilon'=f_k$	ε''_{t^2}	$\varepsilon''=f'_k(=\omega)$	$\varepsilon'''_{r,t}$	$\varepsilon'''_{v^2,t}$	ε'''_{t^3}	ε''''_{t^4}	$v^2-2\beta$	$\dfrac{f'_k}{f_k-1}$	λ
3.9	0.9	14 3	7	—41	39.6	—12	36	—4.7	68	13.4	6.6	6.8
[2	0.4	3.6	4	0	9.6	— 6	18	—9	126	3.2	3.2	0]

The lower series of values refers to the ideal equation of state.

We may add the following remarks to what precedes. According to· (5) we may write for λ:

$$\lambda = \frac{(\alpha^2 - 2\beta)(f_k - 1) - f'_k}{f_k - 1}.$$

The numerator of this is $= (\alpha^2 - 2\beta)(f_k - 1) - (\varepsilon''_{t^2} - \beta'\varepsilon''_{v,t} - {}^1/_6\alpha^2\varepsilon'''_{v^2,t})$, as $f'_k(=\varepsilon'') = \omega$. But as $f_k = \varepsilon'_t$, and $\beta' = \alpha^2 - \beta$, we may also write for this:

$$- \varepsilon''_{t^2} + \alpha^2 \left[(\varepsilon'_t - 1) + \varepsilon''_{v,t} + {}^1/_6 \varepsilon'''_{v^2,t}\right] - \beta\left[2(\varepsilon'_t - 1) + \varepsilon''_{v,t}\right].$$

Now with the ideal equation of state $\lambda = 0$ (see above); and this is what we expected, for then the above form becomes:

$$0 + \alpha^2(3 - 6 + 3) - \beta(6 - 6).$$

Both ε''_{t^2} and the coefficients of α^2 and β are then, namely, $= 0$.

But with the real equation of state the value of this form is :

$$41 + \alpha^2(6 - 12 + 6) - \beta(12 - 12),$$

so that the coefficients of α^2 and β would be again $= 0$. It is not difficult to find a cause for this.

7. If viz. $\dfrac{\partial b}{\partial T} = b'_t$ is very small $\left(\text{just as} \dfrac{\partial b}{\partial v} = b'_v \text{ is slight}\right)$, we may write for $\dfrac{\partial p}{\partial T}$, following from $p = \dfrac{RT}{v - b} - \dfrac{a}{v^2}$, i. e.

$$\frac{\partial p}{\partial T} = \frac{R}{v - b} + \left[\frac{RT}{(v - b)^2} b'_t - \frac{a'}{v^2}\right];$$

$$\frac{\partial p}{\partial T} = \frac{R}{v - b} - \frac{a'}{v^2} = \frac{1}{T}\left[v + \frac{a - Ta'}{v^2}\right] = \frac{1}{T}\left(p + \frac{A}{v^2}\right),$$

so that

$$\frac{\partial^2 p}{\partial v \partial T} = -\frac{2A}{Tv^3} \quad , \quad \frac{\partial^3 p}{\partial v^2 \partial T} = \frac{6A}{Tv^4},$$

in which $A = a - Ta'$, and a' represents $\frac{da}{dT}$. Hence we have at T_k:

$$\varepsilon'_t = \left(\frac{\partial \varepsilon}{\partial m}\right)_{kr} = \left(\frac{T}{p}\frac{\partial p}{\partial T}\right)_{kr} = 1 + \frac{A_k}{p_k v^2_k},$$

and so the well known relation (only now we have A_k instead of a_k)

$$\varepsilon'_t - 1 = \frac{A_k}{p_k v^2_k}.$$

But at T_k we have also, according to what we found just now

$$\varepsilon''_{v,t} = \left(\frac{\partial^2 \varepsilon}{\partial n \partial m}\right)_{kr} = -\frac{2A_k}{T_k v^3_k}\cdot\frac{T_k v_k}{p_k} = -\frac{2A_k}{p_k v^2_k} = -2\,(\varepsilon'_t - 1);$$

$$\varepsilon'''_{v^2,t} = \left(\frac{\partial^3 \varepsilon}{\partial n^2 \partial m}\right)_{kr} = \frac{6A_k}{T_k v^4_k}\cdot\frac{T_k v^2_k}{p_k} = \frac{6A_k}{p_k v^2_k} = 6\,(\varepsilon'_t - 1).$$

So the coefficient of α^2 in the numerator of the above expression for λ passes (with small value of b'_t) really into

$$(\varepsilon'_t - 1) - 2\,(\varepsilon'_t - 1) + (\varepsilon'_t - 1) = 0,$$

the coefficient of β then also passing into

$$2\,(\varepsilon'_t - 1) - 2\,(\varepsilon'_t - 1) = 0$$

That the quantities $\varepsilon'_t - 1$, $\varepsilon''_{v,t}$ and $\varepsilon'''_{v^2,t}$ have *double* the value of those for the ideal equation of state, is owing to this that where the critical pressure is always about $^1/_{27}\,a_k : b_k{}^2$, $\varepsilon'_t - 1$ with $v_k = r b_k$ passes into

$$\varepsilon'_t - 1 = \frac{A_k}{a_k}\cdot\frac{27}{r^2}.$$

In this $A_k : a_k = 1 - (T_k\,a'_k : a_k)$. If now also $T_k\,a'_k$ is small compared with a_k, unity may be written for $A_k : a_k$ by approximation; so that then $\varepsilon'_t - 1$ would become $= 27 : r^2$ for the real equation of state with $r = 2,114 = 27 : 4,5 = 6$, and $= 27 : 9 = 3$ for the ideal equation of state. And as really the value 6 is found for $\varepsilon'_t - 1 = f_k - 1$, a'_k (and also b'_t) *must* really be exceedingly small.

In any case (for small b'_t) $\varepsilon''_{v,t} = -2\,(\varepsilon'_t - 1)$ by high approximation, and hence $= -12$, which is the reason that above we raised the value $-11,4$ found for $\varepsilon''_{v\,t}$ from experimental data to -12. Reversely the slight difference between the two values justifies the supposition that b'_t is really very small. But as then too $\varepsilon'''_{v^2,t} = = 6\,(\varepsilon'_t - 1) = 36$, we have found a sufficient ground in this to raise the value 29,8, i.e. 30, which was calculated from only few experimental data, to 36.

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The numerator of the expression λ now passing into $-\varepsilon''_t$, we get simply :

$$\lambda = -\frac{\varepsilon''_{t^2}}{f_k - 1}, \qquad \qquad \cdots \cdots \cdots \quad (5^n)$$

from which then $\lambda = 40,8 : 6 = 6,8$ follows, as above.

8. As for small b'_t we may write $\dfrac{R}{v-b} - \dfrac{a'}{v^2}$ for $\dfrac{\partial p}{\partial T}$ (see above),

$\dfrac{\partial^2 p}{\partial T^2}$ becomes $= -\dfrac{a''}{v^2}$ (if namely b''_t is also small), hence

$$\varepsilon''_{t^2} = \left(\frac{\partial^2 \varepsilon}{\partial m^2}\right)_{kr} = -\frac{a''_k}{v^2_k}\frac{T_k^2}{p_k}.$$

So we get for λ with $f_k - 1 = \varepsilon_t - 1 = A_k : p_k v^2_k$ (see above) :

$$\lambda = \frac{T_k^2 a''_k}{a_k - T_k a'_k},$$

when we substitute its value for A_k. If we put

$$T_k^2 a''_k : a_k = a''_k, \; T_k a'_k : a_k = a'_k,$$

we get:

$$\lambda = \frac{a''_k}{1 - a'_k} = a''_k,$$

because a'_k must be exceedingly small (see above). As now the value 6,8 was found for λ, this comes to this that a''_k is almost 7, so *great positive* (i. e. $T_k^2 \times (a''_k : a_k)$).

Summarizing everything that we investigated in the above and in previous papers, we come to *this* conclusion that the deviations from the ideal equation of state chiefly find their explanation, besides in the association of the molecules, in the following circumstances:

1. That with small value of $\dfrac{\partial b}{\partial v}$ the value of $\dfrac{\partial^2 b}{\partial v^2}$ is *great*. In consequence of this v_k becomes $= 2,1 b_k$ instead of $v_k = 3 b_k$ for the critical volume.

2. That with small value of $\dfrac{\partial b}{\partial t}, \dfrac{\partial^2 b}{\partial t^2}$, and $\dfrac{da}{dt}$ the value of $\dfrac{d^2 a}{dt^2}$ is *great*. This accounts for the great increase of the characteristic function φ (which has the value 1 at T_k) in the neighbourhood of T_k.

In conclusion we point out that for the determination of the values of ε'''_{v^3} and ε''''_{v^4} the knowledge of the values of b'''_v and b''''_v is required, and so without the complete knowledge of the quantity b as function of v we cannot possibly predict anything regarding the values of ε'''_v and ε'''_{v^4}. That these values are about half the ideal values — from this would follow among others that $v_k^2 b'''_v$ would be not far from 1. *Clarens,* March 1912.