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$$4q + y - 2x + 2 = \frac{4x - 6q}{\sqrt{q - x}}.$$

Introducing z = pq and putting $\sqrt{q-x} = t$ the first and the third equation give

$$2t^{4} + 4t^{3} + Bt^{2} + 4xt + xy + 2x - z = 0$$
$$4t^{3} + 6t^{2} + Bt + 2x = 0$$

therefore the discriminant of the first member of the first equation must be zero.

If we assume

$$24 (xy-z) = A$$

'this may be written

$$(A + B^2)^3 - \{B(3A - B^2) + 216z\}^2 = 0$$

or, after a slight reduction

$$A(A-3B^2)^2 - 432zB(3A-B^2) - 46656z^2 = 0.$$

This solution, though different in form from the former result, represents the same surface; that it passes through the line

$$y = z = 2x$$

may be easily verified.

Physics. — "On some relations holding for the critical point". By
J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In this paper we will derive some important relations which exist between some critical quantities.

If it may be accepted that in the association to multiple molecules no generation of heat (change of energy) takes place, so that q=0 may be put, we saw already in I, p. 291 that the relation

$$f = \left(\frac{T}{p} \frac{dp}{dT}\right)_k = 1 + \frac{a}{p_k v_k^2} \quad . \quad . \quad . \quad (1)$$

holds.

If we now put $v_k : b_k = r$, and substitute for p_k its value, viz. (see I, p. 289)

$$p_k = \frac{1}{27} f_2 \frac{a}{b_k^2},$$

we find:

$$(f-1) r^2 = \frac{27}{f_2} \dots \dots \dots \dots (2)$$

If instead of (1) we write:

$$(77\bar{2})$$

$$f = \frac{p_k + u/v^2}{p_k} = \frac{\alpha_k RT_k}{p_k (v_k - b_k)},$$

in which $a_k = \frac{1+x \beta_k}{1+x}$, and if we substitute the value (see I, p. 288 and 297)

$$RT_k = \frac{8}{27} f_1 \frac{a}{b_k}$$

for RT_k , and further the above values for p_k and v_k , we get:

$$f(r-1) = 8\alpha_k \frac{f_1}{f_2} \dots \dots$$
 (3)

 $From \cdot$

$$\mu = \frac{p_k \, v_k}{RT_k}$$

follows after substitution of the values for p_k , v_k and RT_k :

From (3) and (4) follows also the remarkable relation:

Finally by combination of (2) and (4) we find:

The relations (2), (4), and (6) have also been derived by VANDER WAALS (see among others These Proc. June 1910, p. 118, and those of April 1911, p. 1216 et seq.) in the following form:

$$(f-1) r'^2 = 27$$
; $r's = 8$; $\frac{s^2}{f-1} = \frac{64}{27}$ (all this by approximation).

In this the quantity s is $= 1:\mu$, while r' is not $= v_k:b_k$, but $= v_k:b_q$. In consequence of this our relation (5) is VAN DER WAALS'S relation (he has not taken into account the factor α by the side of RT)

$$\frac{b_k}{b_l} = r' \left(1 - \frac{s}{f} \right).$$

According to (5) $\frac{r-1}{r}$ would namely be $=\frac{s}{f}$ with $a_k = 1$, or r $\left(1 - \frac{s}{f}\right) = 1$. In this $r = v_k : b$: So if we substitute $r' = v_k : b_g$ for r, we get $r'\left(1 - \frac{s}{f}\right) = \frac{b_k}{b_r}$.

It was also already made probable by Van Der Waals (loc. cit.), that $(f-1)r^2 < 27$ and rs < 8, but $s^2 : (f-1)$ almost exactly = 64 : 27.

The theory developed by us confirms these relations perfectly. We found namely in I (p. 297) and II (p. 430 and 431) for the factors f_1 and f_2 :

$$f_1 = \frac{1+x}{1+x\beta_k} \frac{n^2(3m^2-2n)}{m^5} = 1,004 (x=1) \text{ and } 1,010 (x=2)$$

$$f_2 = \frac{(3m^2-2n)^2(4n-3m)}{m^5} = 1,007 (x=1) \text{ and } 1,019 (x=2)$$

See equation (5) in I, p. 288 for the signification of the quantities m and n.

Really $(f-1)r^2 = 27:1,007$ is < 27, but only little smaller; $rs = 8\frac{1,004}{1,007}$ also < 8, but also only little smaller. This holds for x = 1 (partial association to double molecules), but the same holds also for x = 2 (triple molecules).

But we see also that $\frac{s^2}{f-1} = \frac{64}{27} \cdot \frac{(1,004)^2}{1,007}$ is very near $\frac{64}{27}$; also in the case of x=2, where $\frac{f_1^2}{f_2} = \frac{(1,010)^3}{1,019} = 1,001$, just as $\frac{(1,004)^2}{1,007}$. So the value of $s^2:(f--1)$ is only a thousandth of the value higher than $\frac{64}{27}$, viz. 2,3727 instead of 2,3703.

As $\mu = p_k v_k : RT_k$ and $f-1 = a : p_k v_k^2$, we have also

$$\mu^{2}(f-1) = a \cdot \frac{p_{k}}{(RT_{k})^{2}},$$

and so from (6) follows:

$$a = \frac{27}{64} \frac{1}{1,001} \frac{(RT_k)^2}{v_k},$$

which equation together with the equation that follows from (1), viz. $a = (f-1) p_k v_k^2$,

can serve for the determination of a (see also van der Waals, loc. cit.)

introduced by me by the side of μ . So α is evidently $=\frac{27}{8f_1} \cdot \frac{1}{r}$.

¹⁾ I may point out here that the different critical quantities were already expressed by me in experimentally determinable quantities in 1905 in a quite analogous way (see Arch. Teyler 1905 p. 46 and 47) The quantity f was there excluded on account of the possibility that b might be a function of the temperature. For then the fundamental equation (I) no longer holds, as we have proved (1 p. 291). And instead of the quantity $r = v_k : b_k$ the quantity $\alpha = \alpha : RT_kv_k$ was then

Our relations (3) and (5) may effectually be used to calculate a_k , i.e. the state of association at the critical point. Specially (5) is particularly suitable for this purpose, because f_1 and f_2 no longer occur in it. As a_k has been added by us as a factor to RT_k in the equation of state, it can be also decided whether the associated molecules really behave as one molecule as far as their influence on the pressure is concerned, i. e. whether there is real association, or — as van der Waals cautiously expresses it — "quasi-association."

Now we saw in I, p. 295 that β_k must be =0.955 for x=1; and in II, p. 429 that β_k becomes 0.958 for x=2 (in order that f may become =7 and $\mu=0.265$ for T_k). So we find the value $\frac{1.955}{2}=0.977$ for α_k if x=1, and if x=2 the value $\frac{2.916}{3}=0.972$,

so that $f\mu \frac{r-1}{r}$ would have to be = 0.98 à 0.97 and not = 1. Only a very accurate knowledge of the quantities f, μ and $r = v_k$: b_k could decide this.

It follows from (2) and (3) that

$$f = 1 + \frac{27}{f_2} \frac{1}{r^2} = 8\alpha_k \frac{f_1}{f_2} \cdot \frac{1}{r-1}.$$

If we put f_1 and $a_k f_1 : f_2$ both = 1 (for x = 1 $f_2 = 1,007$ and $a_k f_1 : f_2 = 0,977 \times 1,004 : 1,007 = 0,974$), we get by approximation :

$$\frac{8}{r-1} = 1 + \frac{27}{r^2} \dots \dots (7)$$

By approximation this is really fulfilled by values of r in the neighbourhood of 3 (for r=3, where f_1, f_2 and $a_k=1$, (7) would be quite accurately fulfilled). Thus the two members for r=4 become resp. $\frac{8}{3}=2,67$ and $\frac{43}{16}=2,69$; and for r=2 resp. 8 and 7,75.

If we take the factors f_1 , f_2 and a_k into consideration, the first member becomes $= 1 + 27 : (1,007 \times 4,469) = 7,00$ for r = 2,114, and the second member $(= 8 \times 0.9744 : 1,114)$ equally = 7,00 = f.

It is owing to this accidental property of the expression

$$1+\frac{27}{r^2}-\frac{8}{r-1}$$

namely that it differs only very little from zero for values in the neighbourhood of r=3, that the factors f_1 and f_2 differ so little from 1, and that also in the case $v_k:b_k=2$ the expressions RT_k and p_k are again $=\frac{8}{27}\frac{a}{b_k}$, resp. $\frac{1}{27}\frac{a}{b_k^2}$ with close approximation.

With regard to the course of the quantities f, r, and μ for different values of β , we may make the following remarks.

a. With regard to f, given by (see I, p. 294)

$$f = \frac{4n}{4n - 3m},$$

in which (for x = 1)

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

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

(see I, p. 288 and 295), we see immediately that — in view of the fact that m and n assume the value 1 both for $\beta = 1$ and for $\beta = 0$ — this quantity is = 4 for $\beta = 1$ and also for $\beta = 0$. But for intermediate values of β , if φ has only any value (i. e.: if Δb differs from 0), f will be greater than 4 in the neighbourhood of $\beta = 1$, and smaller than 4 in the neighbourhood of $\beta = 0$. Only if $\varphi = 0$, i. e. Δb where = 0, f would be permanently < 4, which is easy to prove from the above expressions for m and n^{-1}). So it follows from this — as f is found = 7 for normal substances — that Δb must necessarily be > 0, if f is to reach so high a value. Accordingly we found in I, p. 295, that β must be = 0.955 and $\varphi = 1.23$ for x = 1, i.e. $\Delta b : b_g$ about 0.7, if we are to get at the same time f = 7 and $\mu = 0.265$. For x = 2 we must have for this $\beta = 0.958$, $\varphi = 0.916$, i.e. $\Delta b : b_g$ about = 0.35 (see II, p. 429).

¹⁾ So the value found by Kamerlingh Onnes for Helium, namely f=2.8, need not be impossible, as van der Waals thinks (These Proc. April 1911, p. 1217). When $\Delta b=0$ (hence b remains constant), f is, as we saw, always <4 for values of β between 0 and 1, which is owing to the factor $\alpha=(1+\beta):2$ by the side of RT (which van der Waals omits; see above). And when Δb has a slight positive value (which may be the case for Helium), and so when b suitably diminishes with v, f will become >4 only near $\beta=1$, but all over the further range between $\beta=$ almost 1 and $\beta=0$ f will be again <4. So it is very well possible that such an association exists for He at the critical point for not too great value of Δb (it need only be slightly greater than the normal association), that f becomes <4.

It remains only to consider whether f can be so much smaller than 4. For $\varphi = 0$ ($\triangle b = 0$), f can decrease to about 3,4 for $\beta = 0.5$; but for $\varphi > 0$ this value can become considerably lower, if β is only sufficiently lower than 1.

Note added during the correction of the Dutch proof. After the above remarks had been written, K.O has carried out some new measurements, and found 4,5 for Helium for f at T_k (These Proc. Dec. 1911, p. 684), so f > 4 also here. But at lower temperatures a considerably lower value is still found, namely f = 3 at the boiling point, so somewhat higher than the former value 2,8 (see above). Now in normal cases f is always about $4 \, ^{10}/_{0}$ lower for m = 0.8 than for m = 1 (6,7 instead of 7); for Helium, however, this would amount to as much as $33 \, ^{10}/_{0}$.

If for x=1 and $\varphi=1,23$ we take the value of 3 only little less than 0,955, e.g. 0,9, we find for f already the value 17,6 with m=1,223, n=0,973. (for $\beta=0,955$ these values were resp. 1,107 and 0,969). [For x=2 this value, though > 7, would be considerably lower].

But if we take $\beta = 0.1$, we find f = 3.6 with m = 1.223, n = 1.271, so again < 4.

Now for the so-called anomalous substances f is really found > 7; for water 7,5 is found, for acetic acid 8, for ethylalcohol 9. So it would follow from this that at the critical point these substances have a value of β , which is < 0.955, resp. < 0.958. But as the curve $f = f(\beta)$ does not intersect the straight line f = 4 until in the neighbourhood of $\beta = 1/3$, β could even be considerably smaller than 0.96. But on no account can β be near 0, because then f would again become < 4.

So for acetic acid, water, alcohol etc. there does exist a *greater* association than for the normal substances at the *critical* point, but most probably not a considerably higher association, and certainly not an almost complete one $(\beta \text{ near } 0)$.

b. The value of r. From (see I, p. 288 and 296)

$$r = \frac{v_k}{b_k} = \frac{3m^2}{3m^2 - 2n}$$

we can easily derive that r is always < 3, when $\beta < 1$ and > 0. With the above values of m and n we find e.g. that r = 2,114 for $\beta = 0,955$; assumes the value 1,77 for $\beta = 0,90$; the value 2,31 for $\beta = 0,1$ (all this with x = 1).

So for abnormal substances a value ≤ 2.1 must be found for r.

c. The quantity μ . From (see I, p. 289 and 294)

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

follows that $\mu=0.375$ for $\beta=1$, but takes the value 0.1875 for $\beta=0$. Further it can be shown that the curve $\mu=f(\beta)$ always hes above the straight line that joins $\mu={}^3/_{16}$ with $\mu={}^3/_8$ for $\varphi=0$ ($\Delta b=0$). This is moreover clear from the above formula (5),

from which immediately follows that then μ is always $> \frac{3}{8} a_k$.

But if $\varphi > 0$ ($\Delta b > 0$), the curve $\mu = f(\beta)$ lies above the said straight line at $\beta = 0$, but falls pretty far below it at $\beta = 1$.

So we find already the value 0,265 for $\beta = 0.955$; the value 0,124 for $\beta = 0.9$; but the value 0,270 for $\beta = 0.1$. (again all this at x = 1, $\varphi = 1.23$).

Hence we shall find a value ≤ 0.265 for μ for abnormal substances. This is actually found. For acetic acid e.g. μ is 0.20, for alcohol we find 0.25.

It is noteworthy that f and μ again approach closely to the ideal values 4 and 0,265 for H_2 , for f we find namely 4,8, and for μ the value 0,34. So this means that then the state of association at the critical point is less than the normal, i. e. $\beta > 0,96$ From formula (5) the value 2,5 would follow for r, which also comes nearer to the ideal value 3.

2. The formula for the vapour pressure at the critical point. From the well known formula (see among others my Thermodynamik in der Chemie p. 59 (1893))

$$\frac{dp_{cx}}{dT} = \frac{1}{v'-v} \int_{v}^{v'} \left(\frac{dp}{dT}\right)_{v} dv$$

follows, as (see p. 290)

$$\left(\frac{dp}{dT}\right)_{v} = \frac{1}{T}\left(p + \frac{a}{v^{2}}\right)$$

for β independent of T(q=0):

$$\frac{dp_{cx}}{dT} = \frac{1}{v'-v} \int_{-v}^{v'} \frac{1}{T} \left(p + \frac{a}{v^2}\right) dv.$$

Hence

$$T \frac{dp_{ca}}{dT} = \frac{1}{v'-v} \int_{0}^{v'} p dv + \frac{1}{v'-v} \int_{0}^{v'} \frac{a}{v^2} dv,$$

or also

$$T\frac{dp_{cx}}{dT} = p_{cx} + \frac{a}{vv'},$$

in which p_{cx} denotes the pressure of coexistence. If henceforth we omit the index cx, we get:

For this we may also write:

$$\frac{m}{\varepsilon}\frac{d\varepsilon}{dm} = 1 + \frac{a}{p_k v_k^2} \frac{dd'}{\varepsilon},$$

or as $a: p_k v_k^2$ is evidently = f - 1, when f denotes the value of $\frac{T}{p} \frac{dp}{dT}$ at the critical point:

$$\frac{d\varepsilon}{dm} - \frac{\varepsilon}{m} = (f-1)\frac{dd'^{1}}{m} \cdot \dots \cdot (9)$$

So this is the most general differential equation, which gives ε as a function of m. But only when d and d' should be perfectly accurately known as functions of m, the integral expression $\varepsilon = f(m)$ can be found.

Now the solution is possible for two extreme cases: 1 in the neighbourhood of the critical temperature, and 2 at low temperatures when the vapour follows the laws of the ideal gases, and the liquid density does not change much any more.

Near the critical temperature

Then
$$d = 1 + a\tau + b\tau^2$$
, $d' = 1 - a\tau + b\tau^2$, hence $dd' = (1 + b\tau^2)^2 - \alpha^2\tau^2 = 1 - (\alpha^2 - 2b)\tau^2$,

when $\tau = 1/1 - m$. (See II, p. 438). If we now put

$$a^2-2b=\gamma,$$

we get accordingly

$$dd' = 1 - \gamma (1-m).$$

If we write further:

$$\varepsilon = 1 - f(1-m) + \frac{1}{2} f'(1-\dot{m})^2$$

then we have:

$$f = \left(\frac{d\varepsilon}{dm}\right)_k; \quad f' = \left(\frac{d^2\varepsilon}{dm^2}\right)_k,$$

because m=1 at T_k , and $\left(\frac{d\varepsilon}{dm}\right)_k = \left(\frac{m}{\varepsilon}\frac{d\varepsilon}{dm}\right)_k$ was denoted by f.

In consequence of this (9) passes into

$$[f-f'(1-m)] - \frac{1-f(1-m)}{1-(1-m)} = (\hat{f}-1)\frac{1-\gamma(1-m)}{1-(1-m)},$$

or in

$$[f-f'(1-m)] - [1-(f-1)(1-m)] = (f-1)[1-(\gamma-1)(1-m)],$$
 from which immediately follows.

¹⁾ From Young's data in his famous summary in the Proc. R. Dublin S. of June 1910 it appears however, that this relation is not accurately satisfied. We find viz. values for $\theta = \left(\frac{m}{\varepsilon}\frac{d\varepsilon}{dm} - 1\right): \frac{dd'}{\varepsilon}$, which increase from 6 (at T_k) to about 9 (at m=0.5). In the neighbourhood of T_k even very rapidly. Thus for C_0H_5F the value of θ is already = 6.23 at m=0.9935; for m=0.9942 we find 6.71 etc. etc. Van der Waals already stated that θ is pictty accurately represented by $\theta=1+\sqrt{1-m}-1/2$ (1-m). We shall, however, this variability, which is also in that form with $\sqrt{1-m}$ an impossibility, leave out of consideration in what follows.

i. e.
$$-f' + (f-1) = -(f-1)(\gamma-1),$$
 or also

$$\underline{\frac{f'}{f-1} = \gamma = a^2 - 2b}, \dots \qquad (10)$$

a very remarkable relation between the quantities $\frac{d\varepsilon}{dm}$ and $\frac{d^2\varepsilon}{dm^2}$ at the critical point, and the coefficients a and b of the densities of the coexisting phases d and d'.

We find for Argon according to Crommelin's data (Comm. 118, p. 9):

$$d-d'=\frac{0,4714}{0,509}$$
 at $1-m=\frac{3,05}{150,7}$,

and as $a = \frac{1}{2}(d-d') : \sqrt{1-m}$, we get:

$$a = \frac{0,4714}{1,018} \sqrt{49,4} = 0,463 \times 7,03 = 3,26.$$

For b, the coefficient of the direction of the straight diameter, has been found

$$b = 0,9027,$$

so that
$$\gamma = a^2 - 2b = 10.63 - 1.81 = 8.8$$
.

The value 5.7 has further been found for f, and by approximation we may calculate:

$$\frac{d\varepsilon}{dm}$$
 at $-123^{\circ}.96 = \frac{5.54}{3.05} \cdot \frac{150.7}{48.0} = 1.82 \times 3.14 = 5.70$

$$\frac{d\varepsilon}{dm}$$
 at $-127^{\circ},66 = \frac{6,61}{4,34} \cdot \frac{150,7}{48,0} = 1,52 \times 3,14 = 4,78$

from

So we find $\frac{0.92}{3.70}$ 150,7 = 38 for $\frac{d^2\varepsilon}{dm^2}$.

This value 38 can of course not lay claim to a high degree of accuracy, because the data are too incomplete for this. If we take a round number 40, we get f':(f-1)=40:4,7=8,5, while we found above about 8,8 for γ . So the agreement is satisfactory.

So for substances where a is about 3,2 (see II p. 437), b = 0.9, f = 7, we should have to find about $f' = 8.4 \times 6 = 50$.

From the data of Fluorbenzene (see Kuenen, die Zustandsgleichung, p. 99) follows $\frac{d\varepsilon}{dm}$ resp. $\frac{0,322}{0,05} = 6,44$, and $\frac{0,206}{0,05} = 4,12$, so $\frac{d^2\varepsilon}{dm^2}$ approximated $=\frac{2,32}{0,05} = 46$, which really gets very near 50 1).

Formula (10), which is quite accurate and of general application, i.e. in the critical point, can therefore render good services — when the quantities f and f' are known from vapour-tension observations near T_k — to calculate the quantity $\gamma = a^2 - 2b$, which renders it possible to calculate accurately the quantity a — which in other circumstances is so difficult to determine experimentally, and which indicates the divergence of the two phases just below T_k — when b is known, i. e. the direction of the straight diameter. Then, however, the direction of this locus should be taken very near T_k , which will probably differ somewhat from the further direction — at least if it is confirmed that very near T_k the straight diameter undergoes an abrupt inflection to the vapour side [Cardoso; see II, p. 437 (read p. 430 last line concave instead of convex side)].

I draw here attention to the fact, that the well-known formula of VAN DER WAALS, viz.

$$-\log \varepsilon = f \frac{1-m}{m},$$

which in this form holds for a large part of the temperature region, is no longer quite accurate in the neighbourhood of T_k . For though this formula then gives the suitable value for $\left(\frac{d\varepsilon}{dm}\right)_k$, it deviates in the second differential quotient. We have namely:

$$\frac{d\varepsilon}{dm} = \varepsilon \frac{f}{m^2},$$

hence:

¹⁾ From Young's tables loc cit. we derive from four successive values of m between 0,9347 and 0,9883 resp. f'=30 and 42. For m=1 f' will draw near to 59. But for a we find at least 3,4, so that γ becomes = 10, and hence f' = 60.

$$\frac{d^2\varepsilon}{dm^2} = f \left\lceil \frac{1}{m^2} \frac{d\varepsilon}{dm} - \frac{2\varepsilon}{m^3} \right\rceil,$$

which becomes for T_k :

$$f' = \left(\frac{d^2 \epsilon}{dm^2}\right) = f(f-2),$$

instead of $f' = (f-1)(a^2-2b)$, as we found above. So according to Van der Waals's formula f' would be $= 7 \times 5 = 35$, whereas really f' is about $= 6 \times 8.5 \text{ à } 10 = 50 \text{ à } 60$.

So according to Van der Waals we should have at T_k :

$$\varepsilon = 1 - f(1-m) + \frac{1}{2}f(f-2)(1-m)^2;$$

and according to our formula:

$$\varepsilon = 1 - f(1-m) + \frac{1}{2}(f-1)(a-2b)(1-m)^2$$
.

Clarens, Dec. 15, 1911.

Anatomy. — "On the relation between the symphysis and the acetabulum in the mammalian pelvis and the signification of the cotyloid bone." By A. J. P. v. d. Broek. (Communicated by Prof. L. Bolk).

In the course of investigations on the structure of the pelvis of Primates I met with some phenomena in the acetabulum, namely the development of the cotyloid bone os acetabuli, that induced us to a comparison with the pelvis of other mammals.

In the Primates the cotyloid bone appears as is pointed out by me¹), in the form of two little triangular bones, an anterior and a posterior one. The anterior cotyloid bone lies between pubis and ilium, the posterior between ilium and ischium. The former excludes the pubis from the acetabulum.

An investigation in the cotyloid bone in other mammals brought to light a distinct correlation between the development of the symphysis and the composition of the acetabulum, which I shall explain in this note. This correlation is, as I think, of some value for our knowledge in the morphologic signification of the cotyloid bone.

In the following explanations I shall divide the pelvis of mammalia after the composition of their symphysis.

I. Symphysis composed by the os pubis and os ischii. In the *Monotremes*, as is known, os pubis and os ischii take the same part in the forming of the symphysis, which is very high. The acetabulum is formed by the three components of the os coxae, namely the os

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