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Prism and interferometer were mounted on the piers cemented to the large brick pier of the laboratory. The tubes are entirely disconnected from the interferometer and mounted on a large iron I girder; this girder is placed upon piers of freestone cemented to large plates of freestone fixed to the wooden laboratory floors. In this manner the adjustment of the interferometer cannot be disturbed by vibrations proceeding from the tubes. At the right of the horizontal projection the four large valves may be seen, by turning which the current was made to flow in either direction through the tube systems.

The mountings containing the glass plates by which the tubes are closed are not given in the Plate. One of these mountings containing the plane parallel plates of glass is drawn to scale in Fig. 3 at one half of the natural size. The four plates of glass are by HILGER, they are circular of 24 m.m. diameter and 10 m.m. thick; in a second series of observations plates 7 m.m. thick have been used. The accuracy of parallelism of the plates is excellent; they are indeed cut from echelon plates. The general plan adopted for the construction of the plate mountings is this: one can only be sure that no change will occur in the position of the plates during the course of an experiment, if this position is *entirely definite*. In order to attain this the glass plate rests upon the inner, accurately grinded, surface of the brass piece *d*. This piece *d* fits accurately into the conical inner part of a piece *b*, itself rigidly screwed to the tube *a*. Parts *d* and *b* are connected by means of the counter nut *c*. The glassplate is held against *d* by the nut *e*. There is no objection to the presence at the *inside* between *e* and *d* of rings of hard india-rubber and of brass. (To be continued)

Physics. — “*A new relation between the critical quantities, and on the unity of all substances in their thermic behaviour.*” (Conclusion). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 24, 1914).

By way of supplement we shall add the calculation of three more isotherms *below* the critical temperature, for which (loc. cit.) data are known from the unsaturated vapour region. If the β -values above T_k were somewhat too high on the whole, now we shall find values which are *much too low*, lower even than β_0 , and therefore impossible. These deviating values can only be explained, when with low temperatures and large volumes *association in the vapour* is assumed.

For then, when RT in the equation of state is made smaller by a factor < 1 , also $v-b$ will be smaller, hence b greater. In this way the too small b -values could therefore be raised to the normal amount. We shall see in the following paragraph that inside the region of coexistence the same phenomenon takes place: the b -values in the vapour much too small (even large negative), the b -values in the liquid phase normal and in harmony with the theory.

Something particular takes therefore place for the large volumes: there is either association in the vapour, or the values of the pressure have been measured too small, or the values of the vapour densities too large. We shall presently return to this.

f. Isotherm of $-130^{\circ},38 = 142,71$ absolute. Hence $m = 0,9473$, $3,424 m = 3,244$.

p	d_A	ε	n	$\varepsilon + 5:n^2$	$n-\beta$	β
12.773	27.394	0.2661	10.873	0.3084	10.518	0.355
28.878	77.821	0.6016	3.827	0.9430	3.440	0.387
						Mean 0.371

Here we should have $\gamma = 0,727$, $\beta_k = 0,415$, $\beta_g = \beta_0 \times 1,475 = 0,421$. Hence the value of β_g found is too low.

g. Isotherm of $-139^{\circ},62 = 133,47$ abs. Here is $m = 0,8860$, $3,424 m = 3,034$.

p	d_A	ε	n	$\varepsilon + 5:n^2$	$n-\beta$	β
11.986	28.122	0.2497	10.591	0.2943	10.308	0.283
14.586	35.573	0.3039	8.373	0.3752	8.085	0.287
						Mean 0.285

With $T = 133,47$ corresponds $\gamma = 0,719$, $\beta_k = 0,411$, $\beta_g = \beta_0 \times 1,457 = 0,416$. The found value of β_g , viz. 0,285, is far below the theoretical value 0,42.

h. Isotherm of $-149^{\circ},60 = 123,49$ abs. For m is found $m = 0,8197$, so $3,424 m = 2,807$.

p	d_A	ε	n	$\varepsilon + 5:n^2$	$n-\beta$	β
11.150	29.183	0.2323	10.206	0.2803	10.014	0.192
12.788	34.646	0.2664	8.597	0.3341	8.401	0.195
Mean						0.194

Here $\gamma = 0,711$, $\beta_K = 0,406$, $\beta_g = \beta_0 \times 1,439 = 0,411$; 0,19 again remains considerably below this.

Combining the found values of β_g in a table and comparing them with the theoretical values, we get the following survey.

m	1.95	1.43	1.13	1.04	1.01	0.95	0.89	0.82
β_g calc.	0.49	0.46	0.43 ⁵	0.43	0.43	0.42	0.42	0.41
β_g found	0.55	0.51	0.45	0.43	0.42	0.37?	0.28?	0.19?

As was already remarked above, the great deviation, especially below $T_k (m < 1)$, must not be ascribed to the theory, but to the experiment, or to association in the vapour.

For the found values of β_g become, as we shall see, even *negative*, hence impossible, at still lower temperatures — while also β_{vap} is continually found *smaller* than β_{liq} , which of course points to something particular in the *vapour*: either association, or inaccurate vapour- or volume determinations, in consequence of a systematic error. (Consult also *g.* of § 18 for a possible explanation.)

18. *The region of coexistence.* (Cf. Comm. 131 and These Proc. of Nov. 1913 (Comm. 138)).

For the calculation of β from the given values of the coexisting vapour and liquid densities it is to be regretted that the vapour pressure observations (see also Comm. 115) have not been made at *exactly* the same temperatures as the density observations. This has rendered interpolations necessary, which of course impairs the perfect accuracy of the ε , which will make its influence felt chiefly on the β -values which are calculated from the *vapour* densities.

In this connection we should not omit mentioning that the value of f , calculated from the first observations of the vapour tensions (Comm. 115), is much too low, viz. 5,712, whereas the much better

value $f > 5,933$ follows from the values given in Comm. 120^a (see p. 10)¹⁾.

We had even sufficient reasons (see § 17) to fix the value of f' at 6 (f could be still *somewhat* larger then).

RANKINE-BOSE's interpolation formula (see These Proc. of Nov. 1913, or Comm. 138), namely

$$\log p = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3},$$

gives by differentiation:

$$\frac{dp}{p dT} = 2,3 \left(-\frac{b}{T^2} - \frac{2c}{T^3} - \frac{3d}{T^4} \right),$$

hence

$$f = \frac{T dp}{p dT} = \frac{2,3}{T} \left(-b - \frac{2c}{T} - \frac{3d}{T^2} \right) = \frac{2,3}{T} \left[634,391 - \frac{61538,13}{T} + \frac{3229392}{T^2} \right].$$

But this formula, which is calculated from all the observations of p (so also from those below $-140^{\circ},80$), and corresponds pretty well with it, gives the value $f_k = 5,628$, which is much too low, at $T_k(150,65)$, hence still lower than the value $f_k = 5,712$, given at the conclusion of Comm. 115, and calculated with $b = -524,3169$, $c = +11343,28$, $d = 0$.

In virtue of this I think I have to recommend caution in the use of the values of p , at least in the neighbourhood of the critical temperature.

We shall now give the following survey of the values found for the densities ϱ_1 and ϱ_2 (Comm. 131), and also the corresponding values of p (Comm. 115, and These Proc. of Nov. 1913 or Comm. 138).

-125°.17	$\varrho_1 = 0.77289$	$\varrho_2 = 0.29534$	$p = 42.457$ (for $-125^{\circ}.49$)
-131°.54	0.91499	0.19432	35.846 ($\rightarrow -129^{\circ}.83$)
-135°.51	0.97385	0.15994	29.264 ($\rightarrow -134^{\circ}.72$)
-140°.20	1.03456	0.12552	22.185 ($\rightarrow -140^{\circ}.80$)
-150°.76	1.13851	0.06785	13.707 ($\rightarrow -150^{\circ}.57$)
-161°.23	1.22414	0.03723	7.4332 ($\rightarrow -161^{\circ}.23$)
-175°.39	1.32482	0.01457	—
-183°.15	1.37396	0.00801	1.3369 ($\rightarrow -183^{\circ}.01$)

We have calculated from ϱ_1 and ϱ_2 the values of d_1 and d_2 , given in the following tables by means of $\varrho_k = 0,53078$.

1) Slightly below T_k , at $-125^{\circ},49$, $f = 2,577 \times 2,3026 = 5,933$ was namely found.

a. $t = -125^{\circ},17$, hence $T = 147,92$, $m = 0,9819$, $3,424m = 3,362$.
By means of linear interpolation $p = 42,944$ has been calculated,
so $\varepsilon = 0,8947$.

d	n	$\varepsilon + 5d^2$	$n - \beta$	β
$d_1 = 1.4563$	0.687	11.50	0.292	0.394 (liq.)
$d_2 = 0.5564$	1.797	2.443	1.376	0.421 (vapour)

As theoretically β ranges from 0,42 to 0,29 (see above), both the values found can be correct.

b. $t = -131^{\circ},54$, $T = 141,55$. Hence $m = 0,9396$, $3,424m = 3,217$. Linear interpolation, giving $p = 33,545$, $\varepsilon = 0,6989$, would be too uncertain here, as $-129^{\circ},8$ differs too much from $-131^{\circ},5$.

VAN DER WAALS' formula $-\log^{10} \varepsilon = f \frac{m}{1-m}$ gives with $f = 2,444^1)$ the value $\varepsilon = 0,6964$.

d	n	$\varepsilon + 5d^2$	$n - \beta$	β
$d_1 = 1.7238$	0.580	15.55	0.207	0.373 (liq.)
$d_2 = 0.3661$	2.732	1.367	2.354	0.377 (vapour)

As β ranges from 0,42 to 0,29, the β -value in the vapour is too small.

c. $t = -135^{\circ},51 = 137,58$ abs. Hence $m = 0,9132$, $3,424m = 3,127$. A linear interpolation gives $p = 28,344$, $\varepsilon = 0,5905$; VAN DER WAALS' formula with $f = 2,420$ gives $\varepsilon = 0,5890$.

d	n	$\varepsilon + 5d^2$	$n - \beta$	β
$d_1 = 1.8348$	0.545	17.42	0.179	0.366 (liq.)
$d_2 = 0.3013$	3.319	1.043	2.998	0.321 (vapour)

¹⁾ The values of f have in each case been calculated by me from the vapour-pressure observations.

The β -value in the vapour begins to be smaller here than that in the liquid!

$d. t = -140^{\circ},20 = 132,89$ abs. Hence $m = 0,8821, 3,424 m = 3,020$. For p we find through linear interpolation $p = 22,795, \varepsilon = 0,4749$; from $-\log^{10} \varepsilon = \text{etc.}$ with $f = 2,415$ on the other hand $\varepsilon = 0,4757$.

d	n	$\varepsilon + 5 d^2$	$n - \beta$	β
$d_1 = 1.9491$	0.513	19.47	0.155	0.358 (liq.)
$d_2 = 0.2365$	4.229	0.7553	3.999	0.230 (v.)

β_n should be about 0,42. Besides 0,23 is again $< 0,36$.

$e. t = -150^{\circ},76 = 122,33$ abs. Hence $m = 0,8120, 3,424 m = 2,780$. Linear interpolation gives $p = 13,595, \varepsilon = 0,2832$.

d	n	$\varepsilon + 5 d^2$	$n - \beta$	β
$d_1 = 2.1450$	0.466	23.29	0.119	0.347 (liq.)
$d_2 = 0.1278$	7.823	0.3649	7.619	0.204 (v.)

The value of β_n is 0,41; 0,20 remains far below this. We moreover point out that also h of § 17 at $t = -149^{\circ},6$ yielded a perfectly harmonious value for the vapour, viz. 0,19. The two series of observations, therefore, cover each other entirely.

$f. t = -161^{\circ},23 = 111,86$ abs. From this $m = 0,7425, 3,424 m = 2,542$. Linear interpolation gives $p = 7,4332, \varepsilon = 0,1549$.

d	n	$\varepsilon + 5 d^2$	$n - \beta$	β
$d_1 = 2.3063$	0.434	26.75	0.095	0.339 (liq.)
$d_2 = 0.07014$	14.257	0.1795	14.167	0.090 (v.)

β_n begins to be more and more impossible. We point out that when $f = 1$ is taken not $= 5$, but e. g. $= 4,95$, the value $\beta_{liq.}$ does not appreciably change: 0,339 then becomes 0,338. But β_v would then become still smaller, viz. 0,07 instead of 0,09).

1) If $p = 7,58$ instead of $= 7,43$, so $\varepsilon = 0,158$ instead of $= 0,155$, we should also have found 0,34 for the value of β in the vapour, the same value at least as that for the liquid. (Also the assumption $\varepsilon_2 = 0,0366$ instead of 0,0372 might lead to the desired purpose).

g. $t = -175^{\circ},39 = 97,70$ abs. Hence $m = 0,6485$, $3,424m = 2,221$. The value of ε interpolated from $-\log^{10} \varepsilon = \text{etc.}$ with $f = 2,322$, gives $\varepsilon = 0,05518$.

d	n	$\varepsilon + 5d^2$	$n - \beta$	β
$d_1 = 2.4960$	0.401	31.21	0.071	0.329 (liq.)
$d_2 = 0.02745$	36.43	0.05894	37.67	-1.24 (v.)

Can the clue to the singular behaviour of the vapour perhaps be found in this that CROMMELIN has not determined the vapour densities *directly*, but that he has calculated them from the law of BOYLE? With a too small value of n one naturally gets then a too slight value of β from $\beta = n - (3,424m : \varepsilon)$. Then no association need of course be assumed in the vapour, and the impossible values of β , below T_k are at once accounted for. The found values of β , would then be quite worthless. The question is therefore: where has CROMMELIN begun not to determine the given values of the vapour density directly, but to *calculate* them from the (not yet valid) law of BOYLE? ¹⁾

h. $t = -183^{\circ},15 = 89,94$ abs. Here $m = 0,5970$, $3,424m = 2,044$. From $\log^{10} \varepsilon = \text{etc.}$ we find the value $\varepsilon = 0,02742$ ($p = 1,3162$) with $f = 2,314$.

d	n	$\varepsilon + 5d^2$	$n - \beta$	β
$d_1 = 2,589$	0.386	33.53	0.061	0.325 (liq.)
$d_2 = 0.01509$	66.26	0.02856	71.57	-5.31 (v.)

We point out that the liquid value duly decreases gradually, and is still higher than $\beta_0 = 0,29$ at $T = 90$ (absolute). So there is nothing impossible here ²⁾.

¹⁾ Otherwise $p = 2,78$ would have to be taken here instead of 2,64, hence $\varepsilon = 0,058$ instead of 0,055; or else q_2 should be assumed somewhat smaller, in order to find at least the value 0,33 (that of the liquid) for β_{vapour} .

²⁾ A rise of p to 1,44 instead of 1,32 (ε to 0,030 instead of 0,0274) — or else a diminution of q_2 from 0,0080 to 0,0075 — might reduce β_0 to 0,33 here. The first supposition is impossible, for then the value of p at $-183^{\circ},15$ would be greater than at $183^{\circ},01$, where 1,34 was found. But a diminution of q_2 by 6% in consequence of an erroneous calculation of q_2 (probably from the law of BOYLE) is very well possible.

Summarizing, we get the following survey for the region of coexistence.

m	0.98	0.94	0.91	0.88	0.81	0.74	0.65	0.60
$\beta_{liq.}$	0.39	0.37	0.37	0.36	0.35	0.34	0.33	0.325
$\beta_v.$	0.42	0.38	0.32?	0.23?	0.20?	0.09?	-1.24?	-5.3?

At the lowest temperature, viz. $t = 89,94$ abs., γ would be about 0,688, and β_v accordingly 0,393, $\beta_\gamma = \beta_0 \times 1,389 = 0,397$, so that β ranges from about 0,40 to about 0,29. The liquid value 0,325 at $n = 0,4$ can be in harmony with this.

In order to examine whether the values of $\beta_{liq.}$ also agree quantitatively with our theory, we will in the first place indicate for the different values of $T(m)$ the corresponding values of n and γ (calculated from $2\gamma - 1 = 0,038 \sqrt{T}$). Besides the value of $v : v_0 = v : b_0 = n : \beta_0$ is given. ($\beta_0 = 0,286$).

m	0.98	0.94	0.91	0.88	0.81	0.74	0.65	0.60	0
n	0.687	0.580	0.545	0.513	0.466	0.434	0.401	0.386	0.286
γ	0.731	0.726	0.723	0.719	0.710	0.702	0.693	0.688	0.5
$v : v_0$	2.40	2.03	1.91	1.79	1.63	1.52	1.40	1.35	1
hence $\beta : \beta_0$	1.33	1.245	1.215	1.18	1.14	1.11	1.08	1.07	1
β calc.	0.381	0.356	0.348	0.338	0.326	0.318	0.309	0.306	0.286
β found	0.394	0.373	0.366	0.358	0.347	0.39	0.329	0.325	(0.305)

The values $\beta : \beta_0 = b : b_0$ have been calculated from the tables of § 16, viz. from those for $\gamma = 0,75$ and $\gamma = 0,70$. We have interpolated for the values of γ given in the above table. On an average the found values of β are 6% higher than the values calculated from our formula (30). If $\beta_0 = 0,30^s$ were taken instead of 0,28^s, the agreement would have been perfect. In connection with this it is remarkable that the *difference* between β_{found} and $\beta_{calc.}$ amounts *almost constantly* to 0,018 or 0,019. The *course* of the β -values is therefore perfectly identical with the course calculated from our formula; identity in the *numerical values* may be obtained by simple change of β_0 from 0,28^s to 0,30^s.

In fact, something is to be said in favour of this. In § 17 we namely calculated the value of β_0 from $2\gamma = b_k : b_0 = \beta_k : \rho_0$, so that $\beta_0 = \beta_k : 2\gamma = 0,429 : 1,5$ became $= 0,286$. But in this it is assumed that the direction of the straight diameter remains the same down to the absolute zero point — which (as we already observed at the conclusion of § 14 (III p. 1051) *cannot* be the case. On the contrary the coefficient of direction will approach to about 0,5 for all substances at low temperatures. It follows from this that the value of the liquid density at $T = 0$, viz. ρ_0 , which is extrapolated from the direction of the so-called straight diameter (*at the critical point*), will always be *too great*, hence v_0 too small, and also $b_0 = v_0$ too small. Accordingly also the value of $\beta_0 = b_0 : v_k$ will be found *too small*, when the inadmissible extrapolation is performed.

The *real* value of β_0 , occurring in our formula (30) for $b = f(v)$, will therefore be always greater than that which occurs in our relations found in I (which are valid *at the critical temperature*). For the calculations of the real β_0 , in order to test our formula (30) by the observations, the calculation from $\beta_0 = \beta_k : 2\gamma_k$ (which is based on this extrapolation) has therefore to be rejected.

The above table need, therefore, give no occasion to conclude to any deviation with respect to the calculated and the found values of β ; the more so as the *course* is perfectly the same, in consequence of the fact that in the relation (30) *not* b , *but* $b - b_0$ *occurs*, so that through simple increase of β to 0,305 the found values of $b - b_0$, resp. $\beta - \beta_0$ will agree perfectly with the values of $\beta - \beta_0$ calculated from our formula.

Remark. We saw that the found values of β_g from the unsaturated gas state (§ 17) were all found *too great* for values of $m > 1$; for values of $m < 1$ all *too small* i. e. larger or smaller than the values of β_g or β_k calculated from our formulae. Also in the region of coexistence ($m < 1$) we found values for β_0 which are all too small, may even negative, hence impossible. Now the too small values may be easily accounted for either by association in the vapour at low temperatures, or through a faulty method of calculation of β_0 from the law of BOYLE (see above). But the too large values of β_g at $m > 1$ *cannot* be accounted for in this way.

It is, however, remarkable, that those too large values of β_g at $m < 1$, combined with the *liquid* values at $m < 1$, seem to obey the relation

$$\beta = 0,4 \sqrt{m}$$

pretty well, as appears from the table on the next page.

$m = 1.95$	1.43	1.13	1.04	1.01	0.98	0.94	0.91	0.88	0.81	0.74	0.65	0.60
$\sqrt{m} = 1.40$	1.20	1.06	1.02	1.005	0.99	0.97	0.95 ⁴	0.94	0.90	0.86	0.80 ⁶	0.77 ⁵
$0.4 \sqrt{m} = 0.56$	0.48	0.42	0.41	0.40	0.40	0.39	0.38	0.38	0.36	0.34	0.32	0.31
β found	0.55	0.51	0.45	0.43	0.42	0.39	0.37	0.37	0.36	0.35	0.34	0.33
						0.36	0.35	0.34	0.33	0.32 ⁵		

The values on the lefthand side of the dividing line might have a somewhat higher factor, viz 0,42, those on the righthand side of the line (the liquid values) a somewhat smaller factor, e. g. 0,39

Yet this relation can hardly satisfy for several reasons. First because the formula $\beta = 0,4\sqrt{m}$ would yield too large values of β_g for larger values of m ; it is at least inconceivable that the increase of b_g with the temperature will continue indefinitely. But secondly the variability with v would disappear through this consideration, and only dependence on T would be assumed. It would then be quite indifferent, whether b was considered at large or at very small volumes. That this, however, is entirely impossible, is at once seen when we bear in mind that only by the assumption $b = f(v)$ we duly get $r < 3$, $s > 3/3$, and $f' > 4$ ¹. Only for "ideal" substances, i. e. at the absolute zero point, can b be independent of the volume.

Other relations could also be derived, among others between the found values of β , $n - \beta$, and m ¹), but they may also be due to chance. We shall, therefore, no longer dwell upon them.

19. The characteristic function.

It is known that for "ordinary" substances the value of the "characteristic" function φ , i. e.

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

in which $f = \frac{m}{\varepsilon} \frac{d\varepsilon_{coer}}{dm}$ is not constantly = 1 — as would have to be the case, when a or b should either not depend on T or only linearly — but with diminishing m increases from 1 to about 1.4 at $m = 0,6$, with about 1,5 as probable limiting value when m approaches to 0. See VAN DER WAALS, and also my Paper in These Proc. of 25 April 1912, p. 1099—1101, in which it appeared that $\varphi = 1 + 6,8(1-m)$ can be put in the neighbourhood of the critical point. (loc. cit. p. 1101).

¹) When e. g. in the region of coexistence for the different values of m we write the corresponding values of n and $n - \beta$, $\frac{\Delta\beta}{\Delta(n - \beta)}$ appears to be about constant, viz. $\pm 0,23$.

For this it is however required that either $\frac{\partial^2}{\partial m^2} \left(\frac{a}{a_k} \right)_k = 6,8$, or $\frac{\partial^2}{\partial m^2} \left(\frac{b}{b_k} \right)_k = -6,5$. (Cf. These Proc. of 3 Sept. 1913, p. 56 and 57).

It is now certainly interesting to consider how this will be, for a substance as Argon, where γ_k is not 0,9, but 0,75.

For the calculation of the values of f I had to make use of RANKINE—ROSE's interpolation formula drawn up by CROMMELIN and treated already above (§ 18). This gives, indeed, the much too low value 5,628 instead of 6 for f_k , but as also the following values of f will possibly be too small in the same degree, there is a chance that the value of the ratio $(f-1):(f_k-1)$ will not differ too much from reality. We then find the following table.

T	m	ε	$d_1 d_2$	$\frac{\varepsilon}{d_1 d_2}$	f	$\frac{f-1}{f_k-1}$	φ
150.65	1	1	1	1	5.628	1	1
147.92	0.9819	0.8947	0.8103	1.104	5.696	1.015	1.12
141.55	0.9396	0.6964	0.6311	1.104	5.869	1.052	1.16
137.58	0.9132	0.5890	0.5529	1.065	5.987	1.078	1.15
132.89	0.8821	0.4757	0.4609	1.032	6.137	1.110	1.15
122.33	0.8120	0.2832	0.4742	1.033	6.534	1.196	1.24
111.86	0.7425	0.1549	0.1618	0.957	7.047	1.307	1.25
97.70	0.6485	0.0552	0.0685	0.805	8.080	1.530	1.23
89.94	0.5970	0.0274	0.0391	0.702	8.945	1.717	1.21

It is certainly remarkable that it would follow from the found values of φ that here too $\left(\frac{\partial \varphi}{\partial m} \right)_k$ would be about -7 , just as for ordinary substances as Fluorbenzene e.g. (see above). For $\left(\frac{\partial \varphi}{\partial m} \right)_k = \frac{0,120}{0,0181} = -6,63$ (whereas it is $-6,8$ for C_6H_5F). But on this head little can be said with certainty, as we have too few observations in the immediate neighbourhood of T_k at our disposal.

The limiting value for $m=0,6$ is now, however, much lower, namely about 1,23 against 1,41 for ordinary substances. Now for

C_6H_6F the value of γ_k is $= 0,95$; hence $b_k : b_0 = 2\gamma_k = 1,90$, and $(b_\eta : b_0)_k = 1,90 \times 1,06 = 2,01$, whereas $\sqrt{2,01} = 1,42$. Further for Argon $\gamma_k = 0,75$, hence $b_k : b_0 = 1,50$ and $(b_\eta : b_0)_k = 1,49 \times 1,018$ (See II, p. 936) $= 1,516$, whereas $\sqrt{1,516} = 1,231$.

It follows from this that with great accuracy

$$\varphi_0 = \sqrt{(b_\eta : b_0)_k} = \sqrt{2\gamma'} \dots \dots \dots (41)$$

may be written for the limiting value at low temperature of the characteristic function φ .

It is therefore again only for "ideal" substances ($b = \text{const.}$) that $\varphi_0 = 1$, and hence φ continually $= 1$ from T_k (then $= 0$) to the absolute zero. But for all the other substances the value of φ will increase from 1 to a limiting value, which will depend on the degree of variability of b .

As according to (36) $(b_\eta - b_0)_k : b_0 = 2\gamma' - 1 = 0,041 \sqrt{T_k}$ (see III § 15), we have also:

$$\varphi_0 = \sqrt{1 + 0,04 \sqrt{T_k}} \dots \dots \dots (41a)$$

We shall not enter any further into this subject, leaving it for a possible later discussion.

In conclusion we shall just repeat what we have already remarked in I, p. 820, that the temperature dependence at extremely low temperatures, where the departures from the equipartition law make themselves felt, undergo a modification. But we shall not enter into this any further either, and we only mention that for Argon the departures from the said law fall entirely within the errors of observation even at 90° absolute (the lowest temperature at which observations have been made). Besides, at those *extremely* low temperatures all substances will probably have passed into the *solid* state, and this state is controlled by other laws than the liquid and the gaseous state, for which our considerations exclusively hold.

20. Conclusion. Though there are still many questions to be answered, and many difficulties left, we may already conclude in virtue of the foregoing to this:

1. The quantity a of VAN DER WAALS' equation of state seems within a large range not to depend on the density, so that the molecular attraction can be represented by $\frac{a}{v^2}$, both in the gaseous and in the liquid state.¹⁾

¹⁾ Cf. also the conclusions in a paper by TYRER in the just published number of the Zeitschr. f. Ph. Ch. (87, Heft 2) p. 195.

2. Whether the quantity α is also independent of the temperature, cannot be stated with perfect certainty yet. For as I think I have fully set forth in my Communications of These Proc. of 25 April 1912 (p. 1091—1106) and particularly of 3 Sept. 1913 (44—59), the assumption of a *large* value either of $\left(\frac{\partial^2 \alpha}{\partial t^2}\right)_k$ or of $-\left(\frac{\partial^2 b}{\partial t^2}\right)_k$ (see p. 56—57 loc. cit.) is necessary for the explanation of the course of the characteristic function φ (see § 19). And as, according to the above, b_q is, indeed, variable with the temperature, but probably not so much that $-\left(\frac{\partial^2 b}{\partial t^2}\right)_k$ gets the required value, besides b possibly also α might depend on the temperature. Only a separate investigation can furnish certainty about this.

3. The quantity b depends both on v and on T . The way in which b depends on v — which is expressed by a formula of the form (see II p. 931 et seq., III p. 1048, formula (29))

$$\left(\frac{b-b_0}{b_q-b_0}\right)^n = 1 - \left(\frac{x}{x_0}\right)^n,$$

in which $x = (b-b_0) : (v-v_0)$, and n depends on the quantity γ , which is in connection with $b_q : b_0$ — leads us to suspect that the variability of b is possibly chiefly a *real* change after all, caused by the action of the pressure $p + a/v^2$ and of the temperature, in an *analogous* way to that which VAN DER WAALS had in mind when drawing up his “equation of state of the molecule”, with which the above expression shows a close resemblance. [cf. also II p. 930—931 (23 April 1914)]. Particularly also with regard to the temperature dependence, viz. [see III p. 1051—1053, formulae (35) to (36)]

$$\frac{b_q-b_0}{b_0} = 2\gamma'-1 = 0,04 \sqrt{T},$$

this agreement is remarkable. But whereas VAN DER WAALS' two exponents n are different, our two exponents are the *same* — and dependent on γ , i. e. on T , so that n can vary from $3\frac{1}{5}$ (for $\gamma = 1$) to ∞ (for $\gamma = \frac{1}{2}$, i. e. $T = 0$), as has been set forth in II, p. 935.

4. It seems to be unnecessary to ascribe the change of b to “quasi association”. It might namely be assumed that the complex molecules possess another volume than the simple ones, and from this a relation $b = f(v)$ might be calculated — according to the known thermodynamic relations which indicate the degree of complexity as function of v and T . RT is then however multiplied by another factor which depends on the degree of association.

What VAN DER WAALS has treated in that sense on p. 1076 of

his Paper in These Proc. of 25 Jan. 1913 (published March 13th), had then already been treated very fully in a series of four papers, written by me at Clarens 1911—1912 (On the variability of b etc.; see These Proc. of 26 Oct., 22 Nov. 1911; 24 Jan., 22 Febr. 1912). That a good deal may be attained in this way can sufficiently appear from these Papers. That difficulties present themselves of the same nature as have been advanced by VAN DER WAALS on p. 1076 at the bottom (loc. cit.), has also appeared at the end of the 4th Paper (p. 716 et seq.).

In any case it is a kind of relief that according to all that proceeds the assumption of quasi association does not seem absolutely necessary. The change namely of b with v and T can very well be explained by other influences.

5. That b_q gradually decreases with the temperature, so that b_q would coincide with b_0 at $T=0$, and accordingly the variability of b would have quite disappeared — in consequence of which we approach more and more to the *ideal* equation of state with constant b , on approaching the absolute zero — this points to the invalidity of the kinetic assumption, that for *very large* volume (for b_q only refers to *large* volumes) i. e. in *ideal gas state*, b_q would be $= 4b_0$. For according to the well known kinetic derivation, b , would then still be $= 4b_0$ at the *lowest temperatures*, whereas it has clearly appeared that b_q approaches more and more to b_0 at low temperatures. Compare particularly III p. 1051, formula (35) and the subsequent eloquent table.

6. Thus after all it would prove true what I wrote in I p. 809 (These Proc. of 26 March 1914), that namely in $v-b$ the quantity b always refers to the real volume of the molecules m and is not $= 4m$, as the kinetic theory would lead us to assume. And in this way the difficulty, which I emphatically pointed out in II, p. 925 (at the bottom)—926, would have naturally vanished.

So it is getting more and more probable that the so-called *quasi* diminution of b does not exist, and that there remains only *real* diminution, which is represented by a formula of the form (29), as far as the dependence on v is concerned, and by a formula of the form (36), as far as the dependence on T is concerned.

Why the earlier kinetic assumption $b_q = 4m$ is really a fiction, and what circumstance has been overlooked then — this I shall demonstrate in a separate Communication.

It will then have become clear that only $v-m$, and not $v-4m$ determines the thermic pressure — which becomes already probable when the kinetic energy of the moving molecules is thought to be

uniformly absorbed by the surrounding medium (see p. 809 of I, already cited above).

7. Hence at bottom the whole thermic behaviour of a substance does not depend *only* on the two quantities a and b , which determine the critical quantities, which in their turn govern the law of the corresponding states — in such a way that all the substances behave correspondingly when they are only considered in equal multiples or sub-divisions of their critical temperature and critical pressure, but also (and the *deviations* from the said law are governed by this) on the *absolute* height of the temperature, at which the substance is considered. According to (36) every substance passes namely through the different types — characterised by the variable ratio $b_g : b_0$, from the type of the “ordinary” substances, where $b_g = b_0$ is about 1,8 ($\gamma = 0,9$) to the type of the “ideal” substances, where b_g is $= b_0$ ($\gamma = 1/2$) — when we descend from the ordinary temperatures to the absolute zero point (see the tables in I, p. 819 and III p. 1052).

The *individuality* of the different substances, which they continue to preserve within the region of the Law of the Corresponding States, is therefore entirely determined by the *real* height of the (absolute) temperature.

Hydrogen at 323° absolute ($T = 10T_k$) will e.g. *on the whole* (Law of Corresponding States) exhibit the same behaviour as Helium at 52° absolute (T also $= 10T_k$) — but H_2 will show a value of about 1,7 for the ratio $b_g \cdot b_0$ at that higher temperature, while He at the same “corresponding” temperature shows a value of about 1.2 for that ratio.

For $v_k : b_k$ we shall find about 2,7 for Hydrogen and Helium at their critical temperature, while $v_k \cdot b_k = 2,1$ is found for an ordinary substance at its critical temperature. Etc. Etc.

And this may suffice for the present. I hope to come back to some *separate* problems later on, which are still awaiting solution. I may mention: the temperature dependence of f (see I, p. 811), the change of direction of the “straight” diameter from T_k to very low temperatures (III p. 1051), the form of the vapour-pressure equation $p = f(T)$, the dependence of the densities of liquid and vapour on the temperature (in connection with the problem of the direction of the straight diameter); and finally the course of the characteristic function in its dependence on T .

But the very first point that will be elucidated in a following Paper is the circumstance mentioned under 6 of the conclusions, that b_g cannot possibly be $= 4m$.

Fontainevent sur Clarens, April 1914.

(September 26, 1914.)