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sound. EINTHOVEN¹⁾ found that third sound in his records as a faint vibration, at a distance of 0,13 sec. from the commencement of the second sound. In our subject, who has a slow heart (from 60 to 70 per minute) I, very often, *but not always*, noted this third sound as a faint diastolic murmur, which *got more distinct when the tube was slipped as far down as 38 c.m.* In fact the venous pulse of this person often, though not always, yielded a beautiful GIBSON "b"-peak in the diastolic portion of the cardiac cycle.

It is evident, therefore, that it is of ventricular origin. If we return again to Fig. 5, the esophagogram of the same subject, and look at wave IV in the diastole at 0,135 sec. after line 4, the place of the closure of the semilunar valves, we shall observe that this place corresponds to the site of EINTHOVEN's third sound.

FRÉDÉRICQ²⁾ also sometimes found a similar diastolic wave in the auricular-pressure tracings.

When putting these facts together, viz. 1 ventricular origin; 2 inconstancy; 3 wave in the auricular-pressure tracings; 4 wave in the esophagogram; 5 wave in the venous pulse curve; GIBSON's explanation seems to me the most plausible. He ascribes the origin of this third sound to the fact that, at a high pressure or at a copious onflow of blood into the veins, the atrio-ventricular valves will close for some moments just before the diastole, on account of the blood rushing into the ventricle during the diastole, in consequence of which the membranes are swung up by the eddies. They produce a short sound and slightly check the blood in its passage to the ventricles.

The evidence presented in this article will, I hope, support the view that, together with the esophageal cardiography, the auscultation and the recording of heart sounds through the esophagus yields results not obtainable through the chestwall.

Physics. — "*A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour.*"

(Continued.) By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of March 28, 1914).

13. If in the found³⁾ expression $b = f(v)$, viz.

¹⁾ W. EINTHOVEN. A third heart sound. Ned Tijdschrift voor Geneesk. 1907 Vol. 2 p. 470.

²⁾ L. FRÉDÉRICQ. La seconde ondulation positive (première ondulation systolique) du pouls veineux physiologique chez le chien. Arch. intern. de Physiol. 1907.

³⁾ These Proc. XVI, p. 924 to be cited as II.

$$\left(\frac{b-b_0}{b_k-b_0}\right)^n = \frac{x_k - b'_k \left(\frac{x}{x_k}\right)^n}{x_k - b'_k}, \quad \dots \quad (30)$$

in which $x = (b-b_0) : (v-v_0)$ — and which except v_0 and $b_0 (=v_0)$ only contains critical quantities which are (directly or indirectly) experimentally determinable — we introduce again b_q-b_0 instead of b_k-b_0 , then when (30b) is taken into account, viz.

$$\left(\frac{b_k-b_0}{b_q-b_0}\right)^n = 1 - \frac{b'_k}{x_k}, \quad \dots \quad (30b)$$

(30) passes into

$$\left(\frac{b-b_0}{b_q-b_0}\right)^n = 1 - \frac{b'_k}{x_k} \left(\frac{x}{x_k}\right)^n.$$

In this is, also according to (30b):

$$x_0^n = \lim \left(\frac{b-b_0}{v-v_0}\right) = x_k^{n+1} : b'_k,$$

so that after substitution the equation (29), i.e.

$$\left(\frac{b-b_0}{b_q-b_0}\right)^n = 1 - \left(\frac{x}{x_0}\right)^n, \quad \dots \quad (29)$$

is found back, from which we had started. In this we have found for the exponent n [see (30a) and (31)]:

$$n = \frac{1 - x_k}{x_k - b'_k} = \frac{8\gamma(\gamma + 1)}{(2\gamma - 1)(4\gamma + 1)} = \frac{2b_k v_k}{(b_k - b_0)(2b_k + b_0)},$$

when for b'_k its value $(b_k - b_0)^2 : b_k v_k$ is substituted, and further for $b_k : b_0$ the value 2γ found in I¹⁾ (see § 6, p 817) and for $v_k : v_0$ the value $2(\gamma + 1)$. In this v_0 is the liquid volume extrapolated from the equation of the straight diameter at $T = 0$, γ being the reduced coefficient of direction of the straight diameter.

In the two foregoing Papers the problem with which I have been continually occupied since 1901, has been brought to a provisional solution. Already then I expressed (Arch. Teyler (2) VII, 3^e partie: "Sur l'influence des corrections etc.") the critical quantities in the values of b'_k and b''_k at the critical point (see among others loc. cit. § 4), and verified the function $b = f(v)$ proposed by KAMERLINGH ONNES for H_2 and CO_2 . We now know that this function does not fulfil the condition that at T_k the quantities b'_k and b''_k must have the values found by me. (See the preceding Paper II.)

In 1905 I went further, and expressed the different critical quantities in two auxiliary quantities α and μ , of which α was in relation with f , and μ represented $1 : s$. (See particularly § 2 of

¹⁾ These Proc. XVI, p 808 to be cited as I.

the article in the Arch. Teyler (2) IX, 3^e partie: "Quelques Remarques sur l'équation d'état").

This is therefore exactly the same as VAN DER WAALS continued years later¹⁾, quite independently of the above investigations, and in which he found several remarkable approximate relations. These were afterwards brought to a more accurate form by me, through the introduction of the quantities λ_1 and λ_2 into the expressions for RT_k and p_k , in which it appeared that $\lambda_1 = \lambda_2$ for ordinary substances amounts to about 0,98, and approaches to 1 as the substances approach more and more to so-called "ideal" substances with b little variable or invariable. (See also I).

Thus all the quantities were expressed in f and s . But in consequence of the equalization of λ_1 and λ_2 all of them could also be expressed in the one quantity f (or rather $f' = f : (1 + \varphi)$ — see I p. 811 and p. 814). This further step was followed by a still more decisive one in consequence of a new relation being found (See I, p. 815 et seq.), on account of which everything could be expressed in the one quantity γ ²⁾, the reduced coefficient of direction of the straight diameter³⁾. For $b_k : v_0$ appeared to be $= 2\gamma$ (p. 816 loc. cit.). Of special importance is the simple relation $f' = 8\gamma$ (p. 818).

The table on p. 819 was the result of these new considerations.

And now that we have also an idea of the course of the function $b = f(v)$ — though of course the found relation (30) or (29) is not the *only* one that satisfies all the imposed conditions, but certainly one of the simplest relations that can be put — now the temperature-influence neglected up to now, forces itself upon our attention. For the found expression (29) only holds for one temperature, viz. for the *critical*. Here too we shall have to be satisfied for the present with an empirical relation, leaving it to future investigation to give the found equations $b = f(v)$ and $b = f(T)$ a theoretical foundation, in which then the relations, found in I between b_k and v_0 (b_0), and those for b'_k and b''_k , will find a natural explanation.

14. The variability with respect to T .

In the expression (30) the quantities $b_k : b_0$ and $v_k : v_0$ occur besides in the first member also in the second member because of x_k and b'_k and the exponent n . In this $b_k : b_0 = 2\gamma$ and $v_k : v_0 = 2(\gamma + 1)$.

¹⁾ These Proc. XIII, p. 118, 1216 et seq.

²⁾ These Proc. XIV, p. 771 et seq.

³⁾ And through which some approximate relations of v. d. W. (These Proc. XV, p. 903, 971 and 1131) which were based on the approximate equality of s and s' (which quantities can, however, differ more than 12%) could be replaced by more accurate ones.

The value of $b_k : b_0$ (and of $v_k : v_0$), i. e. of γ , will depend on the value of the *critical temperature* for *different* substances. But for *one and the same* substance, considered at different temperatures, $b_k : b_0$ (and $v_k : v_0$) loses of course its significance outside T_k . This is, however, not the case with $b_q : b_0$, which quantity is in relation with $b_k : b_0$ through (30^b) at the critical temperature. We have namely :

$$(b_q - b_0)_k = (b_k - b_0) \sqrt[n_k]{\frac{x_k}{x_k - b'_k}}.$$

If in this we substitute the value $2\gamma_k - 1$ for $(b_k - b_0) : b_0$, the value $(2\gamma_k - 1) : (2\gamma_k + 1)$ for $x_k = (b_k - b_0) : (v_k - v_0)$ and the value $(2\gamma_k - 1)^2 : 4\gamma_k(\gamma_k + 1)$ for b'_k — see above, and also I, p. 818 — we find after some reductions :

$$\left(\frac{b_q - b_0}{b_0}\right)_k = (2\gamma_k - 1) \sqrt[n_k]{\frac{4\gamma_k(\gamma_k + 1)}{4\gamma_k + 1}}, \quad . . . \quad (33)$$

in which $n_k = 8\gamma_k(\gamma_k + 1) : (2\gamma_k - 1)(4\gamma_k + 1)$, according to (31) of II.

This naturally suggests the idea of making the above considerations more general by putting $b_q : b_0 \doteq 2\gamma'$; so that not only at the critical temperature the equation (33) holds, in which γ_k represents the reduced coefficient of direction of the straight diameter in the neighbourhood of T_k — but quite general at any arbitrary temperature the relation

$$\frac{b_q - b_0}{b_0} = 2\gamma' - 1 = (2\gamma - 1) \sqrt[n]{\frac{4\gamma(\gamma + 1)}{4\gamma + 1}}, \quad . . . \quad (34)$$

in which, therefore, for an arbitrary substance γ varies together with γ' , when T changes.

Then outside T_k the quantity γ is no longer in relation with any $b_k : b_0$ or with the reduced coefficient of direction of the straight diameter in that point — but yet represents for any arbitrary temperature: the value of $1/2 (b_k : b_0)$, or of the said coefficient of direction, for *another substance for which the critical temperature would correspond with that temperature*. Thus also outside T_k something is left of the original meaning of γ .

So passing from $T = 0$ to $T = \infty$ for *one and the same* substance all the types will be met with, which are found for *different* substances at their critical temperatures. *Every* substance approaches the *ideal* type with constant b , when only the temperature is made to approach to 0, *every* substance approaches the limiting type of the substances with high molecular weight ($\gamma_k = 1$), if only the temperature be taken high enough. This has already been fully explained in I (see § 7, p. 820—821), and there is no call to repeat the explanation here.

Remark.

Before proceeding to the discussion of the dependence on the temperature of γ' and γ , a remark may be made in this context, concerning the necessary consequences of the above considerations with regard to the course of the "straight diameter". When namely for a substance we descend from the critical temperature to lower temperatures, $b_g - b_0$, so also γ , will continually descend; so that the slope of the straight diameter for an arbitrary temperature (which slope at every temperature will depend on the type of the isotherm at the considered temperature, determined there by $b_g - b_0$), will also have to *decrease* from the value γ_k measured at T_k down to the lowest value, i. e. $\gamma = 1/2$, holding for an ideal substance ($T_k = 0$). In other words the straight diameter cannot possibly remain *straight*, but will exhibit such a curvature, that the final direction at $T = 0$ (supposing that liquid volumes could still be realized at these low temperatures) approach to about 0.5.

It is self-evident that the law according to which this decrease takes place *need* not be the same as the law that determines the decrease of γ' or γ with the temperature, since for one and the same substance γ_k at the *critical* temperature is, indeed, in direct relation with the course of the straight diameter there, but this is no longer the case, of course, below the critical temperature, where $b_k : b_0$ and γ have lost their original meaning. A *separate* investigation will have to decide later on, what the relation is of the real direction of the straight diameter below T_k , and the temperature.

That the change of direction for *ordinary* substances will never be very great, however, at least not in the beginning, follows from this that according to the law of variability of γ to be drawn up presently — with which the variation of direction of the straight diameter in any case will run *parallel* — a decrease of γ of any importance will not take place until at *lower* temperature, i. e. at temperatures which are considerably lower than the critical. For substances as Hydrogen and Helium, where the critical temperature lies so near the absolute zero, a *more pronounced* curvature of the straight diameter will of course be expected.

15. *A relation between γ_k and T_k .*

It was then found by me that the quantity γ_k at T_k , i. e. the (reduced) coefficient of direction of the straight diameter, is in a very simple relation to T_k , namely according to the relation

$$\frac{b_k - b_0}{b_0} = 2\gamma_k - 1 = 0,038 \sqrt{T_k}. \quad . \quad . \quad . \quad . \quad (35)$$

It may appear from the following table with what accuracy the value of the quantity γ_k is given by this simple formula.

	T_k	$\sqrt{T_k}$	$2\gamma_k - 1$	γ_k calculated	γ_k found
Helium	5.2	2.28	0.0866	0.543	\pm 0.56
Hydrogen	32.3	5.68	0.2158	0.608	0.604
Argon	150.65	12.27	0.4763	0.738	0.745
Xenon	289.7	17.02	0.6468	0.823	0.813
Acetylene	308.5	17.56	0.6673	0.834	0.858
Isopentane	460.9	21.47	0.8159	0.908	0.914
Fluorbenzene	559.6	23.66	0.8991	0.950	0.933

This table requires some elucidation. Of the many substances whose values were at my disposal, I have only chosen some *typical* ones, namely those substances which, just as in the table in I, p. 819, represent a *class* as far as the value of γ_k is concerned. Oxygen has not been inserted, because we know already from I, p. 819 that according to the values of s and f found for O_2 the value of γ_k would have to be about 0.72, whereas 0.813 was found, just as for Xenon. We have ascribed this to association. Also for CO_2 , which belongs to the class of acetylene, the formula yields too low a value of γ_k , viz. 0.85, whereas 0.9 was found. Whether here too association of the liquid is the cause, is unknown to me. To the iso-pentane group belongs also n-pentane and other substances, of which T_k lies in the neighbourhood of 460° or 470° (absolute), and γ in the neighbourhood of 0.90 or 0.92. For iso-pentane $\gamma_k = 0.916$ according to Young. The value given by us in the table, viz. 0.914, is a mean value. Also C_6H_6 , CCl_4 , and such substances with T_k in the neighbourhood of 550° or 560° absolute, and $\gamma_k = 0.93$ or 0.94 belongs to the Fluorbenzene group. The given value 0.933 is again a mean value.

For H_2O , of which $T_k = 638$, $\sqrt{T_k} = 25.26$, a value 0.98 would follow for γ_k ($2\gamma_k - 1 = 0.96$). It is unknown to me whether experimentally a sufficiently established value of γ_k for water is known; probably it will again be greater than 0.98, because also H_2O is associated, although it be at lower temperatures than the critical.

Even for a substance with a critical temperature of 900° γ_k would

be only 1,07 according to (35). However — at very high temperatures $b_k : b_0$ and so also $b_g : b_0$ will approach to a *limiting value*, so that the coefficient 0,038 for $\sqrt{T_k}$ will probably gradually decrease at higher temperatures. But as yet nothing is known about this, and I shall therefore refrain from giving a more general expression derived from theoretical considerations founded on the calculus of probabilities (statistical mechanics), of which (35) or rather (36) would only be a special case, holding only for temperatures up to about 600° absolute. This expression too is characterized by particular simplicity.

Finally some indications of the sources of the given values of T_k and γ_k (found).

Helium. The value of $T_k = 5,2$ is that of KAMERLINGH ONNES in Comm. 124 (see also Suppl. N° 21). The earlier values given in Comm. 102a, 112, and 119 deviate but little from this final value. The value of γ_k (found) follows from that given for f in Comm. 124, viz. 4,46 as lowest limit. If f is identified with f' , which is certainly permissible here on account of the slight variability of b for Helium, $\gamma_k = \frac{1}{8} f = 0,56$ would follow from $f' = 4,5$. I do not know a direct determination of γ_k .

Hydrogen. In Comm. 119 is given $T_k = 32,3$. From $f = 4,83$ (see KUENEN, die Zustandsgleichung, p. 142) would follow $\gamma_k = 0,604$. I do not know a direct determination of γ_k either.

Argon. According to Comm. 115, $T_k = -122,44 + 273,09 = 150,65$. By direct observation (Comm. 131) $\gamma_k = 0,7446 = 0,745^1)$ was found here.

Xenon. Here I find given $T_k = 16,6 + 273,1 = 289,7$, and further $\gamma_k = 0,813$, as the boundary line coincides entirely with that of O_2 , where $\gamma_k = 0,813$.

We may therefore with close approximation draw up the formula $2\gamma_k - 1 = 0,038 \sqrt{T_k}$ for substances, the critical temperature of which lies no higher than $\pm 600^\circ$ absolute (330° C.), and with extension to arbitrary temperatures:

$$2\gamma - 1 = 0,038 \sqrt{T} \quad . \quad . \quad . \quad . \quad . \quad (35a)$$

For $(b_g - b_0) : b_0 = 2\gamma' - 1$, also holding when a substance is considered at arbitrary temperatures, and not only at the critical, we may put:

$$\frac{b_g - b_0}{b_0} = 2\gamma' - 1 = 0,041 \sqrt{T} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

¹⁾ From $s = 8$ $\gamma_k : (1 + \gamma_k) = 3,424$ (Comm. 131) would follow $\gamma_k = 0,748$, which is in perfect harmony with the found value.

For every value of γ we may calculate the corresponding value of $(2\gamma' - 1) : (2\gamma - 1)$ from (34), bearing in mind that $n = 8\gamma(\gamma + 1) : (2\gamma - 1)(4\gamma + 1)$. We shall then find the mean value 1,08 for that ratio, so that the factor of \sqrt{T} will get an average value of 0,038 (which also represents a mean value) $\times 1,08 = 0,041$.

In this it will no doubt follow from the nature of the thing that the factor 0,041 in the formula for $b_g - b_0$ is the same for all the substances, but the factor 0,038 in the formula for $b_k - b_0$ varies somewhat with different substances, dependent on the value of the ratio $(b_g - b_0) : (b_k - b_0)$. For b_g is, so to say, a *natural* point in the series of values between the final points b_0 and b_g — but b_k only an accidental point, dependent on the situation of the critical point. It follows, however, from this that now, for Helium e.g., the factor for $(b_k - b_0) : b_0$ will become greater than 0,038, viz. 0,041 : 1,004 = 0,041, because for He the value of $(b_g - b_0) : (b_k - b_0) = 1,004$. But this does not present any difficulty, for He can very well have a somewhat greater value of the factor. With 0,041 $2\gamma_k - 1$ would namely become = 0,0931; so $\gamma_k = 0,547$, only little higher therefore than 0,543, and still smaller than 0,56.

For the sake of completeness I shall just give the corrected values of γ_k (calculated) for the other substances mentioned in the table. For H_2 γ_k would become = 0,615. (Here the reduction factor $\theta = (b_g - b_0) : (b_k - b_0) = 1,011$). For Argon we find $\gamma_k = 0,739$ (with $\theta = 1,053$); for Xenon with $\theta = 1,077$ we find the value 0,824 — both almost identical with the values in the original table. C_2H_6 yields $\gamma_k = 0,832$ with $\theta = 1,084$; Isopentane $\gamma_k = 0,897$ with $\theta = 1,11$; Fluorbenzene finally gives $\gamma_k = 0,933$ with $\theta = 1,12$. The last value of γ_k is now also equal to the “found” value of γ_k .

16. Calculation of the theoretical b -values.

The values of b can now be calculated from the reduced equation of state in the form [see I, p. 812, equation (c)]:

$$\left(\varepsilon + \frac{f' - 1}{n^2}\right)(n - \beta) = sm \quad . \quad . \quad . \quad (37)$$

In this β represents $b : v_k$. The values found thus can then be compared with those which we can calculate from (30) and (35). For equation (30) we may write:

$$\left(\frac{b - b_0}{b_0} : \frac{b_k - b_0}{b_0}\right)^n = \frac{1 - \frac{b'_k}{x_k} \left(\frac{x}{x_k}\right)^n}{1 - b'_k : x_k},$$

i. e. with $(b_k - b_0) : b_0 = 2\gamma - 1$; $b'_k = (2\gamma - 1)^2 : 4\gamma(\gamma + 1)$,

$$x_k = (2\gamma - 1) : (2\gamma + 1), \quad x = (b - b_0) : (v - v_0) :$$

$$\left(\frac{b - b_0}{b_0} \cdot \frac{1}{2\gamma - 1} \right) = \frac{1 - \frac{4\gamma^2 - 1}{4\gamma(\gamma + 1)} \left(\frac{b - b_0}{v - v_0} \frac{2\gamma + 1}{2\gamma - 1} \right)^n}{1 - \frac{4\gamma^2 - 1}{4\gamma(\gamma + 1)}}.$$

In this equation $b - b_0$ occurs both in the first and in the second member, and cannot be solved from it (in consequence of n^{th} power). We are therefore obliged to solve $v - v_0$ for the calculation, and then we find after some reductions ($v_0 = b_0$):

$$\frac{v - v_0}{v_0} = \frac{\frac{2\gamma + 1}{2\gamma - 1} \frac{b - b_0}{b_0}}{\sqrt[n]{\frac{4\gamma(\gamma + 1)}{4\gamma^2 - 1} - \frac{4\gamma + 1}{4\gamma^2 - 1} \left[\frac{1}{2\gamma - 1} \frac{b - b_0}{b_0} \right]^n}}, \quad \dots \quad (38)$$

in which $n = 8\gamma(\gamma + 1) : (2\gamma - 1)(4\gamma + 1)$, $2\gamma - 1$ being $= 0,038 \sqrt{T}$.

In order to get an idea about the actual course of the curve $b = f(v)$ according to formula (38), I have taken the trouble — also with a view to testing the calculated values by those which the equation of state will yield for Argon e.g. — to calculate the corresponding values of $(b - b_0) : b_0$ and $(v - v_0) : v_0$ for different values of γ , i.e. of T .

The limiting value b_η for $v = \infty$ is evidently found by putting the denominator of (38) $= 0$, from which follows:

$$\frac{b_\eta - b_0}{b_0} = (2\gamma - 1) \sqrt[n]{\frac{4\gamma(\gamma + 1)}{4\gamma + 1}}, \quad \dots \quad (38a)$$

agreeing with (34).

And with regard to the limiting value $(b - b_0) : (v - v_0)$ for $b = b_0$, $v = v_0$,

$$\lim_{v \rightarrow v_0} \frac{(b - b_0)}{(v - v_0)} = x_0 = x_k \sqrt[n]{\frac{x_k}{b'_k}} = \frac{2\gamma - 1}{2\gamma + 1} \sqrt[n]{\frac{4\gamma(\gamma + 1)}{4\gamma^2 - 1}} \quad (38b)$$

follows immediately from (30b) of I, when instead of γ_k quite generally again γ is written.

a. $\gamma = 0,9$. ($T = \pm 450$ absolute).

For n we find $171 : 46 : 3,7174$, so that (38) etc. passes into

$$\left. \begin{aligned} \frac{v - v_0}{v_0} &= 3,5 \frac{b - b_0}{b_0} : \sqrt[3,7]{\frac{171}{56} - \frac{115}{56} \left[\frac{5}{4} \frac{b - b_0}{b_0} \right]^{3,7}} \\ (b_\eta - b_0) : b_0 &= 0,8 \sqrt[3,7]{171 : 115} \quad ; \quad x_0 = \sqrt[3,7]{171 : 56} \end{aligned} \right\}.$$

This yields the following survey (when for n not the shortened value 3,7, but 3,7174 is taken).

$$(b_g - b_0) : b_0 = 0,8901 \quad ; \quad x_0 = 0,3858$$

$(b-b_0) : b_0 = 0.8$	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$(v-v_0) : v_0 = 2.8 : 1$	2.45 :	2.1 :	1.75 :	1.4 :	1.05 :	0.7 :	0.35 :
	1.1719	1.2582	1.3057	1.3313	1.3438	1.3488	1.3502
$= 2.8$	2.091	1.669	1.340	1.052	0.781	0.519	0.259

Hence we have for $\gamma = 0,9$:

$b : b_0$	1.89	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1
$v : v_0$	∞	3.8*	3.09	2.67	2.34	2.05	1.78	1.52	1.26	1
$\frac{b-b_0}{v-v_0}$	0	0.286	0.335	0.360	0.373	0.380	0.384	0.385	0.386	0.386

It follows from this survey, what is of importance for practical purposes, that the direction of the curve $b = f(v)$ very soon — namely at about $v = 0,6 v_K$ — approaches the final direction given by $(b-b_0) : (v-v_0) = 0,386$. I observed already in II p. 935 that since $b''_0 = 0$, the final part of the curve will have pretty much the *shape of a straight line*. This is actually the case, already for $v : v_0 = 2,34$, where $(b-b_0) : (v-v_0) = 0,373$, the direction does not differ much from the final direction. We introduced just now the quantity v_K marked in this and the following tables by an * ; by this is meant the value of v which *would* correspond with v_K , if the considered substance had its critical temperature at the assumed temperature (here $\pm 450^\circ$). Then namely $\gamma = 0,9 = \gamma_K$, and hence $v_K : v_0 = 2 (\gamma_K + 1) = 3,8$, so that $v = 2,34 v_0$ is then $= 0,6 v_K$.

b. $\gamma = 0,75$. ($T = \pm 150$ absolute).

For n we find 5,25, and further :

$$\frac{v-v_0}{v_0} = 5 \frac{b-b_0}{b_0} : \sqrt[5,25]{\frac{21}{5} - \frac{16}{5} \left(2 \frac{b-b_0}{b_0} \right)^{5,25}} ,$$

$$(b_g - b_0) : b_0 = 0,5 \sqrt[5,25]{21 : 16} \quad ; \quad x_0 = 0,2 \sqrt[5,25]{4,2}$$

giving :

$$(b_q - b_0) : b_0 = 0,5266 \quad ; \quad x_0 = 0,2629$$

$(b-b_0) : b_0 = 0.5$	0.4	0.3	0.2	0.1
$(v-v_0) : v_0 = 2.5:1$	2:	1.5:	1:	0.5:
	1.2486	1.3010	1.3128	1.3143
$= 2.5$	1.602	1.153	0.762	0.380

So we have for $\gamma = 0,75$:

$b : b_0$	1.53	1.5	1.4	1.3	1.2	1.1	1
$v : v_0$	∞	3.5*	2.60	2.15	1.76	1.38	1
$\frac{b-b_0}{v-v_0}$	0	0.200	0.250	0.260	0.2625	0.263	0.263

Here too the curve $b = f(v)$ is almost rectilinear for $v = 0,6 v_k$, nay even for $v = 2,6 v_0 = 0,75 v_k$.

Just as for $\gamma = 0,9$ we see also clearly in the above table, that the greatest change of b will be in the neighbourhood of the critical (or pseudo-critical) point, hence the comparatively large values of b'_k and b''_k , through which $v = v_k$ b_k is reduced from the ideal value 3 to a much lower value, e.g. 2,1 (for $\gamma_k = 0,9$) or 2,33 (for $\gamma_k = 0,75$). We may say that the curve $b = f(v)$ at the beginning and at the end runs almost rectilinearly (at the beginning, between $v = \infty$ and $v = \text{somewhat} > v_k$, parallel to the v -axis), while in the part somewhat before and somewhat past v_k the change of direction takes place from 0 to the final direction given by x_0 (above resp. 0,39 and 0,26).

c. $\gamma = 0,70$. ($T = \pm 100$).

Now $n = 119 : 19 = 6,2632$, and further:

$$\frac{v-v_0}{v_0} = 6 \frac{b-b_0}{b_0} : \left\{ \sqrt[6,26]{\frac{119}{24} - \frac{95}{24} \left(2,5 \frac{b-b_0}{b_0} \right)^{6,26}} \right\},$$

$$(b_q - b_0) : b_0 = 0,4 \sqrt[6,26]{119 : 95} \quad ; \quad x_0 = 1/6 \sqrt[6,26]{119 : 24}$$

from which follows:

$$(b_g - b_0) : b_0 = 0,4146 \quad ; \quad x_0 = 0,2152$$

$(b-b_0) : b_0 = 0.4$	0.3	0.2	0.1
$(v-v_0) : v_0 = 2.4 : 1$	1.8 : 1.2625	1.2 : 1.2891	1.1 : 1.2912
$= 2.4$	1.426	0.931	0.465

In consequence of this we have for $\gamma = 0,70$:

$b : b_0$	1.415	1.4	1.3	1.2	1.1	1
$v : v_0$	∞	3.4*	2.43	1.93	1.465	1
$\frac{b-b_0}{v-v_0}$	0	0.167	0.210	0.215	0.215	0.215

For $v : v_0 = 2,43$, hence $v = 0,7 v_{k'}$, the final direction has already been reached.

d. $\gamma = 0,65$. ($T = \pm 50$).

For n we find the value $143 : 18 = 7,9444$. Further

$$\frac{v-v_0}{v_0} = \frac{23}{3} \frac{b-b_0}{b_0} : \left\{ \sqrt[7,9]{\frac{143}{23} - \frac{120}{23} \left(\frac{10}{3} \frac{b-b_0}{b_0} \right)^{7,9}} \right\},$$

$$(b_g - b_0) : b_0 = 0,3 \sqrt[7,9]{143 : 120} \quad ; \quad x_0 = \sqrt[3]{\frac{7,9}{23} \sqrt[7,9]{143 : 23}}$$

giving

$$(b_g - b_0) : b = 0,3067 \quad ; \quad x_0 = 0,1642$$

$(b-b_0) : b_0 = 0.3$	0.2	0.1
$(v-v_0) : v_0 = 2.3 : 1$	$23/15 : 1.2532$	$23/30 : 1.2586$
$= 2.3$	1.2235	0.609

Hence we have for $\gamma = 0,65$:

$b : b_0$	1.31	1.3	1.2	1.1	1
$v : v_0$	∞	3.3*	2.22	1.61	1
$(b-b_0) : (v-v_0)$	0	0.130	0.1635	0.164	0.164

The final direction is again reached for $v = 0,7 v_k$.

e. $\gamma = 0,60$. ($T = \pm 25$).

The value of n is $192 : 17 = 11,294$. In consequence of this:

$$\frac{v-v_0}{v_0} = 11 \frac{b-b_0}{b_0} : \sqrt[11,3]{\frac{96}{11} - \frac{85}{11} \left(5 \frac{b-b_0}{b_0}\right)^{11,3}},$$

$$(b_0-b_0) : b_0 = 0,2 \sqrt[11,3]{96 : 85} \quad ; \quad x_0 = 1/_{11} \sqrt[11,3]{96 : 11}$$

giving :

$$(b_0-b_0) : b_0 = 0,2022 \quad ; \quad x_0 = 0,1101$$

$(b-b_0) : b_0 = 0.2$	0 1
$(v-v_0) : v_0 = 2 \ 2 : 1 = 2.2$	$1.1 : 1.2114 = 0.908$

so that for $\gamma = 0,60$:

$b : b_0$	1.202	1.2	1.1	1
$v : v_0$	∞	3.2*	1.91	1
$(b-b_0) : (v-v_0)$	0	0.091	0.110	0.110

A little beyond v_k the deviation of the final direction is already unimportant.

f. $\gamma = 0,55$. ($T = \pm 5$).

Here n is $= 341 \cdot 16 = 21,3125$, and further:

$$\frac{v-v_0}{v_0} = 21 \frac{b-b_0}{b_0} : \sqrt[21,3]{\frac{341}{21} - \frac{320}{21} \left(10 \frac{b-b_0}{b_0}\right)^{21,3}},$$

$$(b_0-b_0) : b_0 = 0,1 \sqrt[21,3]{341 : 320} \quad ; \quad x_0 = 1/_{21} \sqrt[21,3]{341 : 21}$$

from which follows:

$$(b_0-b_0) : b_0 = 0,1003 \quad ; \quad x_0 = 0,05428,$$

so that we find (e.g. for a *Helium* isotherm at its critical temperature):

$b : b_0$	1.1003	1.1	1
$v : v_0$	∞	3.1*	1
$(b-b_0) : (v-v_0)$	0	0.0476	0.0543

And finally for $\gamma = 0,50$ ($T = 0$), where b is invariable, we should find $b:b_0=1$ for all values of $v:v_0$, $(b-b_0):(v-v_0)$ always being $= 0$.

Let us in conclusion review according to what law or approximate law the found value of x_0 — i. e. of the final direction of the curve $b=f(v)$ — varies with γ or T .

From (38b) follows $x_0 = (2\gamma-1) \times \frac{1}{2\gamma+1} \sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma^2-1}}$. We shall see that here the factor of $2\gamma-1$ is almost constant between $\gamma = 0,75$ and $\gamma = 0,55$.

$\gamma = 0.90$	0.75	0.70	0.65	0.60	0.55	0.50
$x_0 = 0.386$	0.263	0.215	0.164	0.110	0.0543	0
$x_0:(2\gamma-1) = 0.482$	0.526	0.538	0.547	0.551	0.543	0.5

If 0,482 for $\gamma = 0,9$ and 0,5 for $\gamma = 0,5$ is excepted, the mean value of the other values is 0,541, and we may therefore write with some accuracy:

$$\lim \left(\frac{b-b_0}{v-v_0} \right)_0 = 0,54 (2\gamma-1).$$

But seeing that $2\gamma-1 = 0,038 \sqrt{T}$, we have also:

$$\lim \frac{b-b_0}{v-v_0} = 0,02 \sqrt{T}, \quad (39')$$

which according to the above will therefore also hold *all along the final part* of the curve $b=f(v)$, from values of $v = 0,7 v_k$ to $v = v_0$.

For Argon at temperatures $\geq T_k$ only $\gamma = 0,75$ ($T = 150$) and $\gamma = 0,70$ ($T = 100$) should practically be taken into account, because the observations have not been carried further than $T = 90$ (absolute). If we thus consider an isotherm for Argon below the critical point, we may assume that (provided it be not *too* near T_k) the value of b will practically agree with b_g at the *vapour* volume, and that at the *liquid* volume the b -value will satisfy the above equation (39).

If (39) is written in the reduced form

$$\lim \frac{(b:v_k)-(v_0:v_k)}{(v:v_k)-(v_0:v_k)} = 0,02 \sqrt{T},$$

and if it is taken into account that $b:v_k = \beta$, $v:v_k = n$, and $v_0:v_k = n_0 = \beta_0 = 1:2(1+\gamma_k)$, then for Argon:

$$(\beta - \frac{2}{7}) : (n - \frac{2}{7}) = 0,02 \sqrt{T}, \quad (n < 0,7) \quad . . . (40)$$

when $\gamma_k = 0,75$ is taken.

As $1 - (\beta - \frac{2}{7}) : (n - \frac{2}{7})$ also $= (n - \beta) : (n - \frac{2}{7})$, we may also write:

$$n - \beta = (n - \frac{2}{7})(1 - 0,02 \sqrt{T}), \quad (n < 0,7) \quad (40a)$$

in which $n - \beta$ is determined by the equation of state (37). Equation (40a) may serve among others to determine the dependence of the reduced liquid volume on the temperature at low temperatures.

17. Calculation of the b -values from the isotherms of Argon.

In order to be able to draw up the reduced equation of state of Argon, we must in the first place accurately know the critical data. For the critical density ρ_k I took the value 0,53078 from Comm. Leiden 131 (MATHIAS, KAMERLINGH ONNES and CROMMELIN). Abbreviated therefore 0,531. In this it is assumed that the straight diameter remains straight up to the critical point. The values of CROMMELIN in Comm. 115 ($\rho_k = 0,509$) and Comm. 118^a ($\rho_k = 0,496$) are both too low.

For T_k has been taken $-122^{\circ},44\text{C} = \underline{150,65}$ absolute, and for p_k the value 47,996, shortened to 48,0 — both from Comm. 115.

* For s we assumed the value $s = 3,424$ from Comm. 131. In Comm. 120a (KAMERLINGH ONNES and CROMMELIN) a too low value, viz. 3,283, has been given (in connection with the too slight critical density).

At last the value of f . We derive from Comm. 120^a $f > 2,577 \times 2,3026$, hence $f > 5,933$. (Comm. 115 gives the too low value 5,712). From $s = 8f' : (8 + f')$ — see I, formula (7) — would follow $f' = 5,986$. And from $f' = 8\gamma$ — see I, formula (17) — follows with $\gamma = 0,7446$ the value $f' = 5,957$. Now $f = f'(1 + \varphi)$ — see I, formula (5) — hence, as φ is small positive, f slightly greater than f' . We may therefore safely conclude to the value 6,00 for f from the two values 5,99 and 5,96 for f' , which also fulfils the condition $f > 5,93$.

Comm. 131 gives $0,0026235 T_k : \rho_k$ as reduced coefficient of direction for the straight diameter, giving with the above given values of T_k and ρ_k the value $\gamma = 0,7446$. We saw just now that this value yields a good value for f' . From $s = 8\gamma : (1 + \gamma)$ would follow $\gamma = 0,748$ for γ . The former value from Comm. 120a, viz. $0,003050 T_k : \rho_k = 0,9027$, is much too high, and would be quite in contradiction with our temperature-relation $2\gamma - 1 = 0,038 \sqrt{T}$, which yields 0,738, in good harmony with 0,745, but not in harmony with 0,903, which high value of γ would belong to substances of the Isopentane type with a critical temperature of about 450 absolute, i.e. three times as high as that of Argon.

We see from this how useful the above table in § 15, in con-

junction with that in I, p. 819, can be for a first orientation concerning the critical data.

Now the equation of state (37) passes into (assuming the value 6 also for f'')

$$\left(\varepsilon + \frac{5}{n^2}\right)(n-\beta) = 3,424 m,$$

from which may be solved.

$$\beta = n - \frac{3,424m}{\varepsilon + 5:n^2}.$$

The following values have all been derived from Comm. 118b, p. 19 et seq. (KAMERLINGH ONNES and CROMMELIN) and from these Proceedings of Oct. 1913 p. 477 et seq. (CROMMELIN). (See also Comm. 138).

The value β_k follows from $r = v_k : b_k = 1 : \beta_k$, hence $\beta_k = 1 : r$. Now $r = (1+\gamma) : \gamma$ — see I, formula (14) — so that $\beta_k = \gamma : (1+\gamma) = 0,427$. With $r = 1 + 8 : f''$ (see I, (7)) follows with $f'' = 6$ for r the value 2,33, hence for β_k the value $3/7 = 0,429$. As further $2\gamma = b_k : b_0 = \beta_k : \beta_0$, we have $\beta_0 = \beta_k : 2\gamma = 0,429 : 1,5 = 0,286$.

We are not yet ready to carry out the calculations, as the given volumes must all be changed into "reduced" volumes. Now $\varrho = 0,1073$ corresponds with $d_A = 60,21$, (Comm. 118, p. 8), so $\varrho = 0,5308$ (the critical density, corresponding to $n=1$) would correspond to $d_A = 297,84$, i. e. to $V_A = 1 : 297,84$. This is therefore the value of V_A at the critical point. To reduce this to 1 ($n=1$), this and all the other volumes must be multiplied by the factor 297,84.

a. The isotherm of $20^\circ,39$ C, i. e. (with $T_0 = 273,09$) $T = 293,48$ absolute. From this follows $m = 293,48 : 150,65 = 1,948$, so $3,424 m = 6,670$, so that

$$n - \beta = 6,670 : (\varepsilon + 5 : n^2).$$

Now e. g. $d_A = 20,499$ has been given (for $p = 21,783$). So the value V_A is $1 : 20,499$, hence according to the above $n = 297,84 : 20,499$. We must therefore divide 297,84 by all the given values of d_A . Thus we calculate the following survey.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
21.783	20.499	0.4538	14.529	0.4775	13.969	0.560
34.487	32.590	0.7185	9.139	0.7784	8.570	0.569
49.604	47.319	1.0334	6.294	1.1597	5.752	0.542
61.741	59.250	1.2863	5.027	1.4842	4.494	0.532
Mean						0.551

From (35) with $\sqrt{T} = \sqrt{293,5} = 17,13$ would follow $\gamma = 0,825$, referring to a substance which would have its critical temperature at 293,5. Then (see above) β_k would be $= \beta_0 \times 2\gamma = 0,471$, while $\beta_g = \beta_0 \times 1,708$ would be $= 0,488$. [See *a.* and *b.* of § 16; 1,708 for $\gamma = 0,825$ is the mean value of 1,8901 for $\gamma = 0,9$ and 1,5266 for $\gamma = 0,75$].

The above found values of β (which will probably practically agree with β_g) are all higher than the value of β_g calculated from our formula.

b. The isotherm of $-57^{\circ},72$; i. e. $T = 215,37$, $m = 1,430$, and so $3,424 m = 4,895$. From $n - \beta = 4,895 : (\varepsilon + 5 : n^2)$ the following table is calculated.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
17.872	23.509	0.3723	12.669	0.4035	12.131	0.538
35.127	48.116	0.7318	6.190	0.8623	5.677	0.513
46.209	64.948	0.9627	4.586	1.2005	4.078	0.508
62.079	90.695	1.2933	3.284	1.7569	2.786	0.498
Mean						0.514

Just as above we can again fix the limits of β , corresponding to a temperature of 215 absolute. With $\sqrt{T} = 14,68$ corresponds $\gamma = 0,779$; hence $\beta_k = 0,445$, $\beta_g = \beta_0 \times 1,597 = 0,456$. Again β , calculated from the equation of state, is higher than the value calculated from our formula.

c. Isotherm of $-102^{\circ},51 = 170,58$ absolute. Then $m = 1,132$, hence $3,424 m = 3,8770$.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
14.864	25.571	0.3097	11.648	0.3466	11.188	0.460
32.394	62.240	0.6749	4.785	0.8932	4.340	0.445
40.976	84.002	0.8537	3.546	1.2513	3.099	0.447
51.398	115.88	1.0708	2.570	1.8276	2.121	0.449
62.239	158.01	1.2967	1.885	2.6938	1.434	0.451
Mean						0.450

With $T = 170,6$ corresponds $\gamma = 0,748$, $\beta_k = 0,427$, $\beta_g = \beta_0 \times 1,522 =$

$= 0,435$. The β -values from the equation of state are still somewhat too high.

d. The isotherm of $-116^{\circ},62 = 156,47$ absolute. This yields $m = 1,039$, hence $3,424 m = 3,556$.

p	d_A	z	n	$z + 5:n^2$	$n - \beta$	β
13.863	26.480	0.2888	11.248	0.3287	10.824	0.424
37.250	90.563	0.7760	3.289	1.2429	2.867	0.422
50.259	159.71	1.0471	1.865	2.4992	1.427	0.438
54.922	210.02	1.1442	1.418	3.6551	0.976	0.442
60.669	331.29	1.2639	0.8990	7.5120	0.475	0.424

Mean 0.430

With $T = 156,5$ corresponds $\gamma = 0,738$, yielding $\beta_k = 0,422$, $\beta_g = \beta_0 \times 1,500 = 0,429$. As, just as in the above tables, $n > 1$ (the last value is a little smaller), no appreciable diminution of the limiting value β_g can be expected for β yet. Now that we approach the critical temperature of Argon, however, the mean value 0,48 found in the table (calculated from the equation of state) agrees with the theoretical value of β_g which can be calculated from our formula.

e. The isotherm of $-121^{\circ},21 = 151,88$ absolute, so slightly above the critical temperature. Here $m = 1,008$, hence $3,424 m$ becomes $= 3,452$.

p	d_A	z	n	$z + 5:n^2$	$n - \beta$	β
13.754	27.326	0.2865	10.899	0.3290	10.497	0.402
30.122	71.459	0.6275	4.168	0.9183	3.765	0.403
37.465	100.33	0.7805	2.969	1.3536	2.556	0.413
45.282	148.95	0.9434	2.000	2.2064	1.569	0.431
49.865	234.13	1.0389	1.272	4.1596	0.833	0.439
50.885	333.75	1.0601	0.8924	7.4013	0.468	0.424

Mean 0.419

With $T = 151,88$ corresponds $\gamma = 0,734$, $\beta_k = 0,419$, $\beta_g = \beta_0 \times 1,491 = 0,426$. The found mean value, though slightly too small, agrees pretty well with it.

Fontainvent sur Clarens, March 1914.

(To be concluded).