Physics. — *"A new relation between the critical quantities, and on the unity of all substances in their thermic behaviour."* (Continuation.) By J. J. van Laar. (Communicated by Prof. H. A. Lorentz.)

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

8. *The shape of the function* $b=f(v)$. After we have thus derived some relations in the preceding paper [1], by means of which all the critical quantities are expressed in the one quantity γ, the reduced coefficient of direction of the so-called "straight diameter", we shall examine what forms of $b=f(v)$ satisfy the relations found.

These relations, from which the table on p. 829 loc.cit. has been calculated, are the following. [Cf. also the formulae (14) and (21) loc.cit. p. 818].

$$\left.\begin{array}{l} z=\dfrac{b_k}{v_0}=2\gamma \quad ; \quad r=\dfrac{v_k}{b_k}=\dfrac{1+\gamma}{\gamma} \quad ; \quad s'=\dfrac{v_k}{v_0}=2(1+\gamma) \\ s=\dfrac{RT_k}{p_kv_k}=\dfrac{8\gamma}{1+\gamma} \quad ; \quad \dfrac{s'}{s}=\dfrac{(1+\gamma)^2}{4\gamma} \quad ; \quad \lambda=\dfrac{27\gamma^2}{(1+\gamma)^2(8\gamma-1)} \end{array}\right\} \quad . \quad (22)$$

In this λ is the factor in

$$RT_k=\frac{8}{27}\lambda_1\frac{a}{b_k} \quad ; \quad p_k=\frac{1}{27}\lambda_2\frac{a}{b_k^2},$$

in which $\lambda_1=\lambda_2=\lambda$ is put. The found values of λ_1 and λ_2 appeared, namely, not to differ, and λ is always in the neighbourhood of unity. Though γ varies from 0,9 for "normal" substances to 0,5 for "ideal" substances, λ ranges only between the values 0,98 and 1.

We further found:

$$\left.\begin{array}{l} f'=\dfrac{f}{1+\varphi}=8\gamma \quad ; \quad b'_k=\dfrac{(2\gamma-1)^2}{4\gamma(\gamma+1)} \quad ; \quad 1-b'_k=\dfrac{8\gamma-1}{4\gamma(\gamma+1)} \\ -\beta''_k=-\dfrac{v_kb''_k}{1-b'_k}=\dfrac{f'-4}{f'}=\dfrac{2\gamma-1}{2\gamma} \end{array}\right\} \quad . \quad (23)$$

In this $\varphi=\dfrac{r}{r-1}\beta'_t$, in which $\beta'_t=\dfrac{T_k}{v_k}\left(\dfrac{\partial b}{\partial T}\right)_k$. We saw that β'_t is generally exceedingly small.

We may still remark that the relations for b'_k and b''_k may also be written thus:

$$b'_k=\frac{(b_k-v_0)^2}{b_k\,v_k} \quad ; \quad -b''_k=\frac{b_k-v_0}{b_k\,v_k}(1-b'_k) \;, \quad . \quad . \quad . \quad (24)$$

[1]) These Proc p. 808.

which enables us to find out something about the course of the function $b=f(v)$. For the sake of accuracy the original v_0 is everywhere written in the above formulae, and not the b_0 put equal to it. The quantity v_0 is namely the liquid volume at $T=0$ extrapolated from the equation of the straight diameter. From $\frac{1}{2}(d_1+d_2)-1=\gamma(1-m)$ follows namely, when $d_2=0$ and $m=0$, that the reduced limit of density $(d_1)_0$, i.e. $v_k:v_0$, becomes equal to $s'=2(1+\gamma)$. It is this v_0 which occurs in the above relations.

In virtue of the fact that when the limiting volume of b corresponding to this limiting volume v_0, i.e. b_0, is assumed different from v_0, very intricate, if not impossible results are obtained for $b=f(v)$ — whereas the assumption $b_0=v_0$ leads to comparatively simple results, I have been led to identify b_0 with v_0. So we assume that at the limiting value of v for $T=0$ (calculated from the formula of the straight diameter) also $b=v$, and so also $p=\infty$. Hence what we call v_0 and b_0 in what follows is the same as VAN DER WAALS understands by v_{lim} and b_{lim} [1]) — with this difference, however, that $\left(\frac{db}{dv}\right)_0$ is *not* $=1$, but always much smaller than 1, and will even appear to be $=0$ (at $\gamma=\frac{1}{2}$). That the latter is really the case, follows also from this, that in the limiting case $\gamma=\frac{1}{2}$ (ideal substances) — where therefore $b_g=b_0$, and the course of the function $b=f(v)$ is represented by a *straight line* parallel to the v-axis — necessarily b'_0 must be $=0$.

Let us now proceed to determine the shape of the function $b=f(v)$. According to what was observed in § 1 of the foregoing paper, we consider the variation of b, with the volume entirely as an *apparent change*, and that chiefly on the ground of the joint action of two influences, the diminution of the factor 4 in $b_g=4m$ ($m=$ nucleus volume of the molecules) to about $2m$ at b_0 — at least at the ordinary temperatures; and the simultaneously acting influence of temporary molecule aggregations (quasi association). These two influences will make the quantity b in $v-b$ diminish from $4m$ to about $2m$.

But at very low temperatures, at which b_g will approach more and more to b_0 (see § 7 loc. cit.) till $b_g=b_0$ at $T=0$, this variability disappears — and the question rises how this is possible. Does $b_0=2m$ then rise to $b_g=4m$, or does $b_g=4m$ descend to

1) These Proc XV p. 1132 at the top, 1138 and p. 1142 at the top, where everywhere $v_{lim}=b_{lim}$ is assumed. On p 1138 also $v_{lim}=v_0$ (from the straight diameter) is put. Our v_0 and b_0 are therefore exactly the same quantities as VAN DER WAALS' v_{lim} and b_{lim}.

$b_0 = 2m$. The former is in contradiction with the experimental result that b_g, and so also b *decreases* with decrease of temperature; the latter seems in opposition to the theoretical result that for infinitely large volume b_q must always be $= 4m$, and cannot possibly therefore assume the value $2m$, however low the temperature may be.

Yet the latter is the only possible supposition. We shall return to this at the close of this paper, and we shall then propose a supposition which may be alleged as an explication of this apparently so singular behaviour.

9. Let us first consider the forms which present themselves most readily, but cannot satisfy the equations (24), in connection with the convergency to b_0 and v_0.

When we put generally:

$$b = b_g - \alpha f\left(\frac{v}{\beta}\right), \quad \ldots \ldots \quad (a)$$

in which $f(v)$ is such that this function becomes $= 0$ for $v = \infty$, and increases with decreasing v, then

$$b_k = b_g - \alpha f\left(\frac{v_k}{\beta}\right),$$

hence also

$$b = b_g - (b_q - b_k)\frac{f(v)}{f(v_k)}, \quad \ldots \ldots \quad (b)$$

when we briefly write $f(v)$ for $f\left(\frac{v}{\beta}\right)$.

From this follows:

$$b' = -\frac{b_q - b_k}{\beta}\frac{f'(v)}{f(v_k)} \quad ; \quad b'' = -\frac{b_q - b_k}{\beta^2}\frac{f''(v)}{f(v_k)},$$

hence

$$b'_k = \frac{b_q - b_k}{\beta}\;\frac{-f'(v_k)}{f(v_k)} \; ; \quad -b''_k = \frac{b_q - b_k}{\beta^2}\frac{f''(v_k)}{f(v_k)},$$

therefore

$$\frac{-b''_k}{b'_k} = \frac{1}{\beta}\;\frac{f''(v_k)}{-f'(v_k)}.$$

But as according to (24) also

$$\frac{-b''_k}{b'_k} = \frac{1 - b'_k}{b_k - b_0}$$

we have necessarily:

$$\beta = \frac{b_k - b_0}{1 - b'_k}\;\frac{f''(v_k)}{-f'(v_k)} \quad \ldots \ldots \quad (c)$$

In consequence of this we have:

$$b'_k = \frac{b_g - b_k}{b_k - b_0}(1 - b'_k)\frac{(-f'(v_k))^2 : f''(v_k)}{f(v_k)},$$

from which follows for the relation $(b_g - b_k) : (b_k - b_0)$:

$$\frac{b_g - b_k}{b_k - b_0} = \frac{b'_k}{1 - b'_k}\frac{f(v_k)}{(-f'(v_k))^2 : f''(v_k)} \quad . \quad . \quad . \quad . \quad . \quad (d)$$

The equation (b), written in the form:

$$b - b_k = (b_g - b_k)\left(1 - \frac{f(v)}{f(v_k)}\right),$$

then becomes:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\frac{f(v_k) - f(v)}{(-f'(v_k))^2 : f''(v_k)}, \quad . \quad . \quad . \quad (e)$$

in which b'_k in given by (24).

First Example.

$$f(v) = e^{-v/\beta}.$$

Then $f'(v) = \partial f(v : \beta) : \partial(v : \beta) = -e^{-v/\beta}$, and $f''(v) = e^{-v/\beta}$, so that we obtain:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\frac{e^{-v_k/\beta} - e^{-v/\beta}}{e^{-v_k/\beta}},$$

as $(-f'(v_k))^2 : f''(v_k) = e^{-v_k/\beta}$

Hence we get:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\left[1 - e^{\frac{v_k - v}{b_k - b_0}(1 - b'_k)}\right], \quad . \quad (25)$$

as β according to $(c) = (b_k - b_0) : (1 - b'_k)$.

But the equation (25) — which in the neighbourhood of the critical point of course perfectly accurately satisfies the conditions: 1) that at $v = \infty$ the value of b becomes properly b_g in connection with (d), and 2) that the equation at v_k for b'_k and b''_k gives the values determined by (24) — is quite deficient in the neighbourhood of v_0. It has, namely, also to satisfy there for *small* values of $b_k - b_0$, when γ is near $^1/_2$ (ideal substances). Now in this case with $b'_k = (b_k - b_0)^2 : b_k v_k$ (see (24)), and in regard of the circumstance that in consequence of b'_k becoming $= 0$, unity may be written for $1 - b'_k$, for $v = v_0$, $b = b_0$ we get:

$$\frac{b_k - b_0}{b_k - b_0} = \frac{(b_k - b_0)^2}{b_k v_k} e^{\frac{v_k - v_0}{b_k - b_0}},$$

in which within [ ] 1 has been omitted by the side of the infinitely large value of the exponential quantity. But now the first member of this equation $=1$, the second member becoming $=0 \times e^{\infty}$, hence approaching ∞. Not until $v_k - v_0$ should be of the order $b_k - b_0$, by which the exponential quantity could be made of the order $b_k v_k . (b_k - b_0)^2$, could the above equation be satisfied. But then v_0 would get into the neighbourhood of v_k, when $b_k - b_0$ approaches to 0, i.e. when γ approaches to $^1/_2$, and this is impossible.

It is easy to see from the graphical representation that the indicated $f(v)$ intersects the v-axis already soon after v_k, in consequence of which b passes to negative values, so that there can be no question of a convergency to the point v_0, b_0.

And it is easy to see that this cannot be changed by changes in the form of the chosen exponential function. Nor can KAMERLINGH ONNES' function satisfy. For this function, viz.

$$b = b_q - (b_q - b_0) e^{-\alpha(v-v_0)} ,$$

leading after substitution of v_k and b_k, through which v_0 and b_0 are eliminated, to

$$b = b_g - (b_q - b_k) e^{-\alpha(v-v_k)},$$

is identical with (b), when $e^{-v/\beta}$ is substituted for $f(v)$, (α satisfy is then $= {}^1/_\beta$),. For it would inevitably lead to the rejected equation (25).

And if this and suchlike functions are made to satisfy at v_0, b_0 — they will necessarily *not* satisfy at v_k, b_k, i.e. the values b'_k and b''_k will then entirely differ from the theoretical values indicated by (24).

Second example.

$$f(v) = \left(\frac{v}{\beta}\right)^{-\theta}$$

As β will disappear here, an exponent θ must still be added to satisfy the conditions (24), which exponent can then again be determined from (c), b_q being given by (d).

We now find:

$$-f'(v) = \theta \left(\frac{v}{\beta}\right)^{-(\theta+1)} \quad ; \quad f''(v) = \theta(\theta+1) \left(\frac{v}{\beta}\right)^{-(\theta+2)} ,$$

and hence for $(-f'(v_k))^2 : f''(v_k)$ the value $\dfrac{\theta}{\theta+1} \left(\dfrac{v_k}{\beta}\right)^{-\theta}$.

In consequence of this (e) becomes:

$$b \quad b_k = (b_k - b_0) \frac{b'_k}{1-b'_k} \frac{\theta + 1}{\theta} \left[1 - \left(\frac{v_k}{v}\right)^\theta\right], \quad . \quad . \quad . \quad (26)$$

in which θ is determined through (c). (c) now becomes namely:

$$\beta = \frac{b_k - b_0}{1 - b'_k} (\theta + 1) \left(\frac{v_k}{\beta}\right)^{-1},$$

yielding

$$\theta + 1 = (1 - b'_k) \frac{v_k}{b_k - b_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26a)$$

But here too there is no convergency for v_0, b_0. For small values of $b_k - b_0$ (26) namely approaches to

$$\frac{b_k - b_0}{b_k - b_0} = b'_k \left(\frac{v_k}{v_0}\right)^{\frac{v_k}{b_k - b_0}},$$

because $1 - b'_k$ and $(\theta + 1) : \theta$ then approach to 1, while between [ ] again 1 has been omitted by the side of $(v_k : v_0)^\theta$, which approaches to infinite. The first member is $= 1$, the second member approaching to $0 \times a^\infty$, hence to ∞.

Also when $(v - v_0)^{-\theta}$ had been assumed, we should have found the same impossibility, even still intensified, because then $(v_k : v_0)^{v_k : (b_k - b_0)}$ would have become $[(v_k - v_0) : (v_0 - v_0)]^{(v_k - v_0) : (b_k - b_0)}$, because of which the root of the power would approach ∞ for all the values of $b_k - b_0$ [1]).

In the same way the functions may be tested, in which $v : (b - b_0)$ is written instead of $v : \beta$. The functions $-f(v)$ and $f''(v)$ then become somewhat more intricate, but the divergency at v_0, b_0 continues to exist.

And as for VAN DER WAALS's equation in the general form

$$\frac{b - b_0}{v - b} = f \left[1 - \left(\frac{b - b_0}{b_g - b_0}\right)^n\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

the so-called "equation of state of the molecule" — this leads to such complicated expressions for f and n, in order to satisfy the relations (24), that no physical significance can possibly be assigned to these expressions. Also when $v - v_0$ is substituted for $v - b$. We shall, therefore, enter no further into all these calculations, and leave their execution to the reader.

Before leaving this kind of functions, which all lead to failures, I will just point out that if one should want e.g. to derive from the

1) Also the supposition $f(v) = \left(\frac{\beta}{v_0} - \frac{\beta}{v}\right)^\theta - \left(\frac{\beta}{v_0}\right)^\theta$ leads to the same impossibilities.

relations (24) by division, that also *outside* the critical point

$$-\frac{b''}{1-b'}=\frac{b'}{b-b_0},$$

one would easily find back (25) after integration of this differential equation. But we know that this equation does not satisfy. Also other obvious suppositions about b'' and b', which satisfy (24) at the critical point, lead to such impossible final results.

10. We have now come to the forms, which lead to possible, and at the same time not too intricate results, also as far as the convergency point v_0, b_0 is concerned. In all these forms the relation $(b-b_0):(v-v_0)$ or also $(b-b_0):(v-b)$ occurs by the side of $(b-b_0):(b_g-b_0)$. In this respect the *general* form of VAN DER WAALS's relation (27) is the best that can be assumed. Here everything is reached that can be desired. The relation $(b-b_0):(v-b)$ approaches to a finite limiting value f at $v=b=v_0$, when in the second member $b=b_0$, so that the convergency at v_0, b_0 has been properly warranted beforehand. Further b becomes $b=b_g$ for $v=\infty$. But as has been said before — in order properly to obtain the values given by (24) at v_k, *exceedingly intricate* expressions must be assigned to f and n, in which for the case $b=$ constant, i.e. b_k-b_0 or $b_g-b_0=0$ ($\gamma={}^1/_2$) f approaches to 0 and n to ∞.

This is of course in itself nothing particular, as it is e.g. by no means necessary that, as VAN DER WAALS desires, $Lim\,(b-b_0):(v-v_0)$, is $=1$ or assumes another finite value; it can very well become $=0$, as for values of v close to v_0 (or b) b can long have assumed a value close to the limiting value b_0. This is the more apparent when we consider the case that b no longer changes at all, or hardly changes (at $\gamma={}^1/_2$). The value of b can then be put about $=b_0$ throughout its course, from $v=\infty$ to $v=v_0$, so that the numerator of $(b-b_0)\cdot(v-v_0)$ approaches much more rapidly (or infinitely more rapidly) to 0 than the denominator. Nor is a very large value for n with small values of b_k-b_0 impossible in itself.

But it is the exceeding intricacy of the expressions for f and n that make us reject equation (27) in *that* form. And these intricate results remain, so long as the exponent of $(b-b_0):(v-b)$, which is always $=1$ in (27), *differs* from that of $(b-b_0):(b_g-b_0)$, viz. n.

Let us take generally:

$$\left(\frac{b-b_0}{v-v_0}\right)^{\theta}=f\left[1-\left(\frac{b-b_0}{b_g-b_0}\right)^{n}\right], \quad . \quad . \quad . \quad ; \qquad (27^a)$$

and let us then calculate f and n for given value of θ. It soon appears then that simplication is only found *when* $\theta = n$. The reader may be left to ascertain this fact for himself.

Accordingly we shall only treat the case that $\theta = n$ is put in (27^a) from the beginning. But first one more remark.

The equation ($27a$) is a special case of the general assumption:

$$b = b_g - (b_g - b_0)\frac{f(v)}{f(v_0)},$$

in which $f(v)$ approaches to 0 for $v = \infty$. We may, however, also write for this:

$$b - b_0 = (b_g - b_0)\left(1 - \frac{f(v)}{f(v_0)}\right),$$

or still more general:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{f(v)}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

when $f(v_0) = Lim\, f(v)$ is denoted by a for $v = v_0$. If we now take for $f(v)$ the *special* function $[(b - b_0) : (v - v_0)]^\theta$. this passes into:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{1}{a}\left(\frac{b - b_0}{v - v_0}\right)^\theta,$$

which corresponds with ($27a$), because a means the same thing as f. We can, therefore, consider VAN DER WAALS's form as a special case of the quite general form (28), when namely, $(b - b_0) : (v - v_0)$ is simply taken for $f(v)$, and not this ratio to a certain power, while also VAN DER WAALS substitutes $v - b$ for $v - v_0$.

But whereas VAN DER WAALS's form with $n = 2$, $\theta = 1$, $f = 1$ or more, has a physical meaning, being related to the deformation of the molecule by pressure and temperature (which deformation in our theory — see § 1 of the preceding paper — may be considered negligible, and has, therefore, been left out of account), our formula is for the present without such a significance, and it must only be considered as an *empirical* relation — just as many others, e.g. the equation of the straight diameter, that for the vapour pressure, etc. — to which possibly afterwards a physical meaning can be assigned, in relation with the different factors which give rise to a *quasi* variation of b.

So we put:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{1}{a}\left(\frac{b - b_0}{v - v_0}\right)^n, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

in which $a = Lim\left(\frac{b - b_0}{v - v_0}\right)^n$ at $v = v_0$, $b = b_0$; while $b_0 = v_0$ is assumed.

If for the sake of brevity we write x for $(b-b_0):(v-v_0)$, then

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

which with introduction of v_k and b_k passes into

$$\left(\frac{b_k-b_0}{b_q-b_0}\right)^n = 1 - \frac{x_k^n}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

from which b_q can be computed, when a and n are known. Substitution yields:

$$\left(\frac{b-b_0}{b_k-b_0}\right)^n = \frac{a-x^n}{a-x_k^n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29a)$$

in which a is therefore $Lim\ x_0^n$. Let us derive from this the values of b' and b''. We find for b':

$$\frac{b'}{b_k-b_0}\, n \left(\frac{b-b_0}{b_k-b_0}\right)^{n-1} = -\frac{nx^{n-1}}{a-x_k^n}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right),$$

hence for b'':

$$\frac{b''}{b_k-b_0}\, n\left(\frac{b-b_0}{b_k-b_0}\right)^{n-1} + \frac{(b')^2}{(b_k-b_0)^2}\, n\,(n-1)\left(\frac{b-b_0}{b_k-b_0}\right)^{n-2} =$$

$$= -\frac{n\,(n-1)\,x^{n-2}}{a-x_k^n}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right)^2 -$$

$$-\frac{n\,x^{n-1}}{a-x_k^n}\left[2\frac{b-b_0}{(v-b_0)^3} - 2\frac{b'}{(v-b_0)^2} + \frac{b''}{v-b_0}\right]$$

Hence at the critical point after multiplication by b_k-b_0, resp. $-(b_k-b_0)^2$:

$$\left.\begin{aligned} b'_k &= x_k^{n-1}\frac{x_k^2 - b'_k\, x_k}{a-x_k^n} \quad ; \quad - b''_k\,(b_k-b_0) - (n-1)\,(b'_k)^2 = \\ &= \frac{(n-1)\,x_k^{n-2}\,(x_k^2-b'_k\,x_k)^2 + x_k^{n-1}\,[2x_k^3-2b'_k\,x_k^2 + b''_k\,(b_k-b_0)\,x_k]}{a-x_k^n}\end{aligned}\right\}.$$

The first equation yields at once:

$$b'_k\left(1+\frac{x_k^n}{a-x_k^n}\right) = \frac{x_k^{n+1}}{a-x_k^n},$$

hence $b'_k \, . \, a = x_k^{n+1}$, or

$$a = \frac{x_k^{n+1}}{b'_k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

The second gives:

$$- b''_k\,(b_k-b_0)\left(1+\frac{x_k^n}{a-x_k^n}\right) - (n-1)\,(b'_k)^2 =$$

$$= \frac{(n-1)(b'_k)^2 x_k^n - 2(n-1)\,b'_k\,x_k^{n+1} - 2b'_k\,x_k^{n+1} + (n-1)x_k^{n+2} + 2x_k^{n+2}}{a-x_k^n},$$

hence:

$$-b''_k(b_k-b_0)a-(n-1)(b'_k)^2(a-x_k^n)=(n-1)(b'_k)^2x_k^n-2nb'_k\,x_k^{n+1}+(n+1)x_k^{n+2}.$$

As according to (24) $-b''_k(b_k-b_0)=(b_k-b_0)^2(1-b'_k):b_k v_k$, i. e. $=b'_k(1-b'_k)$, we have also:

$$[b'_k-(b'_k)^2]\,a=(n-1)(b'_k)^2\,a-2nb'_k\,x_k^{n+1}+(n+1)\,x_k^{n+2},$$

or

$$n\,(b'_k)^2\,a-b'_k\,a-2n\,b'_k\,x_k^{n+1}+(n+1)\,x_k^{n+2}=0.$$

After substitution of x_k^{n+1} for $b'_k a$, and division by x_k^{n+1}, we get:

$$nb'_k-1-2n\,b'_k+(n+1)\,x_k=0,$$

or

$$(n+1)\,x_k-nb'_k=1,$$

from which

$$n=\frac{1-x_k}{x_k-b'_k}\quad\ldots\ldots\ldots\ldots\quad(\gamma)$$

On account of the value found for a, we can now write for $(29a)$:

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

or also

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

in which

$$x=\frac{b-b_0}{v-b_0}\;;\quad x_k=\frac{b_k-b_0}{v_k-v_0}\;;\quad b'_k=\frac{(b_k-b_0)^2}{b_k\,v_k}\;;\quad n=\frac{1-x_k}{x_k-b'_k},\quad.\quad(30a)$$

while from (α), (β) taken into consideration, follows:

$$\left(\frac{b_k-b_0}{b_g-b_0}\right)^n=1-\frac{b'_k}{x_k}\quad;\quad x_0{}^n=a=\frac{x_k^{n+1}}{b'_k}\quad\ldots\quad(30b)$$

11. It is easily seen that the found equation (30) fulfils all conditions. In the first place we get properly

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

for $v=\infty$ $(x=0)$, which is in harmony with (30^b). Secondly the first member $=1$ for $v=v_k$ $(x=x_k)$, the second member $(x_k-b'_k):(x_k-b'_k)$ also becoming $=1$. Thirdly for $b=b_0$, $v=v_0$ the first member $=0$, and the numerator of the second member $=x_k-\dfrac{b'_k\,a}{x_k^n}$, as $x_0{}^n=a$ is put. But $b'_k\,a=x_k^{n+1}$, hence this numerator is also $=0$.

By differentiation of (30), considering that there b'_k stands for

$(b_k - b_0)^2 : b_k v_k$, which we shall call β for a moment, we find further:

$$n\left(\frac{b-b_0}{b_k-b_0}\right)^{n-1}\frac{b'}{b_k-b_0}=\frac{1}{x_k-\beta}\left(-\frac{\beta}{x_k^n}nx^{n-1}\right)\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right),$$

which becomes for v_k:

$$b'_k=\frac{\beta}{x_k(x_k-\beta)}(x_k^2-b'_k x_k)=\beta\frac{x_k-b'_k}{x_k-\beta},$$

from which immediately follows $b'_k=\beta$, i.e. the value given by (24). And with regard to b''_k, from

$$-\frac{b'}{b_k-b_0}\left(\frac{b-b_0}{b_k-b_0}\right)^{n-1}=\frac{\beta}{x_k^n(x_k-\beta)}x^{n-1}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right) \quad (a)$$

follows after a second differentiation, and substitution of $v=v_k$ and $b=b_k$ (see also above):

$$-b''_k(b_k-b_0)-(n-1)b'^2_k=\frac{\beta}{x_k^n(x_k-\beta)}\Big[(n-1)x_k^{n-2}(x_k^2-b'_k x_k)^2+$$
$$+x_k^{n-1}[2x_k^3-2b'_k x_k^2+b''_k(b_k-b_0)x_k]\Big],$$

yielding, when β is written for b'_k:

$$-b''_k(b_k-b_0)\left(1+\frac{\beta}{x_k-\beta}\right)=(n-1)\beta^2+\beta\Big[(n-1)(x_k-\beta)+2x_k\Big],$$

or $$-b''_k(b_k-b_0)x_k=\beta(x_k-\beta).(n+1)x_k.$$

Now according to (30a) $(n+1)(x_k-\beta)=(1-x_k)+(x_k-\beta)=1-\beta$; hence

$$-b''_k(b_k-b_0)=\beta(1-\beta)=b'_k(1-b'_k),$$

and now (24) is again satisfied.

After having thus carried out these control calculations, we return to equation (30).

The quantity b'_0 cannot be computed from the above equation (a) for b', as the latter gives $0=0$ for v_0, b_0. No more could b''_0 be calculated from the general equation for b''. But since in the neighbourhood of v_0, b_0:

$$x=\frac{b-b_0}{v-v_0}=b'_0+{}^1\!/_2\,b''_0(v-v_0)+\ldots$$

evidently $b'_0=Lim\,\dfrac{b-b_0}{v-v_0}=x_0$, and hence according to (30b) $=\sqrt[n]{a}$.

When we represent $(b-b_0):(b_k-b_0)$ by δ,

$$b'_0\delta^{n-1}=\frac{\beta}{x_k^n(x_k-\beta)}x^{n-1}\left(\frac{x^2}{\delta}-\frac{b'_0x}{\delta}\right)$$

follows from the above equation (α) for b'; or also, since x^n approaches $x_0{}^n = a = x_k{}^{n+1} : b'_k$, and $\beta = b'_k$:

$$b'_0 \delta^n = \frac{x_k}{x_k - b'_k}(x - b'_0) \; .$$

Now $x - b'_0 = {}^1/_2\, b''_0 (v - v_0)$, hence:

$$b''_0 = 2b'_0 \delta^n \frac{x_k - b'_k}{x_k} \frac{1}{v - v_0} ,$$

or also

$$b''_0 (b_k - b_0) = 2(b'_0)^2 \delta^{n-1} \frac{x_k - b'_k}{x_k} ,$$

since $(b_k - b_0) : (v - v_0) = ((b_k - b_0) : (b - b_0)) \times ((b - b_0) : (v - v_0)) = \delta^{-1} \times b'_0$.

With assumption of (30) the value of b''_0 is therefore always $= 0$, since δ approaches to 0. The final course of the curve $b = f(v)$ is therefore straight, the coefficient of direction being indicated by $b'_0 = \sqrt[n]{a}$.

That for $v = \infty$, in consequence of $v - v_0$ in the numerator of x, both b'_g and b''_g become $= 0$, is self-evident.

Let us now examine the values of a and n for different values of $b_k - b_0$ or of γ.

When we substitute in $n = (1 - x_k) : (x_k - b'_k)$ the values of x_k and b'_k, we get:

$$n = \frac{1 - \dfrac{b_k - b_0}{v_k - v_0}}{\dfrac{b_k - b_0}{v_k - v_0} - \dfrac{(b_k - b_0)^2}{b_k v_k}} ,$$

or also, taking the relations (22) into account, i. e. $b_k : b_0 = 2\gamma$, $v_k : v_0 = 2(1 + \gamma)$, in which $b_0 = v_0$:

$$n = \left(1 - \frac{2\gamma - 1}{2\gamma + 1}\right) : \left(\frac{2\gamma - 1}{2\gamma + 1} - \frac{(2\gamma - 1)^2}{4\gamma(\gamma + 1)}\right) ,$$

i. e.

$$n = 8\gamma(\gamma + 1) : (2\gamma - 1)\left[4\gamma(\gamma + 1) - (2\gamma + 1)(2\gamma - 1)\right] ,$$

or

$$n = \frac{8\gamma(\gamma + 1)}{(2\gamma - 1)(4\gamma + 1)} = \frac{2b_k v_k}{(b_k - b_0)(2b_k + b_0)} \quad . \; . \; . \quad (31)$$

So the exponent n ranges from $3^1/_5$ (when $\gamma = 1$) to ∞ (when $\gamma = {}^1/_2$). For ordinary substances ($\gamma = 0{,}9$) n becomes $= 46 : 171 = 3{,}72$; for Argon ($\gamma = 0{,}75$) $n = 5{,}25$.

For the value of a, i. e. the limiting value x_0 of $(b-b_0):(v-v_0)$ for $v=v_0$, $b=b_0$, we find from $x_0^n=a=x_k^{n+1}:b'_k$ (see 30^b) the value:

$$x_0=\sqrt[n]{a}=x_k\sqrt[n]{\frac{x_k}{b'_k}}=\frac{2\gamma-1}{2\gamma+1}\sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma^2-1}}, \quad . \quad . \quad (32)$$

in which n possesses the value given by (31). This limiting value x_0, which is at the same time $=b'_0$ (see above) assumes for $\gamma=1$ the value:

$\frac{1}{3}\sqrt[3^1/_5]{\frac{8}{3}}={}^1/_3\times 1,359=0,453$, for $\gamma=0,9$ the value $\frac{0,8}{2,8}\sqrt[3,72]{\frac{6\ 84}{2\ 24}}={}^2/_7\times 1,350=\underline{0,386}$; for $\gamma=0,75$ the value $\frac{0,5}{2,5}\sqrt[5^1/_4]{\frac{5,25}{1,25}}={}^1/_5\times 1,314=0,263$; while for $\gamma=0,5$ it properly approaches 0 ($b-b_0$ then namely has become continually $=0$). For $\sqrt[n]{(x_k:b'_k)}$ then approaches unity, the factor $(2\gamma-1):(2\gamma+1)$ approaching to 0.

Accordingly for all "ordinary substances", where γ is about 0,9, the line $b=f(v)$ will approach the point of convergency v_0,b_0 at an angle of about 21° ($tg\ \varphi=0,39$).

In conclusion we will still discuss the value of $b_q:b_k$ according to (30^b), viz.

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

The limiting value of this for $\gamma=1$ is evidently $\sqrt[3^1/_5]{\left[{}^1/_3:({}^1/_3-{}^1/_8)\right]}=\sqrt[3^1/_5]{1,6}=1,158$, which with $b_k:b_0=2$ leads to $b_q:b_k=1,079$. For ordinary substances ($\gamma=0,9$) we find $\sqrt[3,72]{\left[{}^2/_7:({}^2/_7-{}^8/_{35,5})\right]}=$ $=\sqrt[3,72]{(171:115)}=1,113$, leading with $b_k:b_0=1,8$ to $b_g:b_k$ $=\underline{1,050}$, i. e. the normal value. For Argon ($\gamma=0,75$) the second member becomes $\sqrt[5,25]{\left[{}^1/_5:({}^1/_5-{}^1/_{21})\right]}=\sqrt[5,25]{(21:16)}=1,053$, which with $b_k:b_0=1,5$ for $b_q:b_k$ yields the value 1,018. Finally for an ideal substance $b_q:b_k=1$.

Equation (30) found by us, therefore, yields good results in every respect, from $v=\infty$ to $v=v_0$, and that for all values of b_k-b_0 or of γ. In addition it may once more be stated, that when $b=b_0$ in the first member, the second member too must be $=0$, hence $x_k=b'_k(x_0:x_k)^n$, in consequence of which $a=x_0^n$ assumes the value

$x_k^{n+1} : b'_k$, thus properly the value given by (30^b). It is also easy to see that in the limiting case $\gamma = {}^1/_2$, i.e. $b_k = b_0$, the equation (30) passes into $b = const. = b_0$. For then $b'_k = 0$, and the second member becomes constantly $= 1$, i.e. b constant $= b_k = b_0$.

12. It is self-evident that the equation (30) is not the only one that will satisfy the different conditions. Thus in the second member of (29) e. g. we might have assumed $v - b$ in the denominator instead of $v - v_0$. A calculation quite analogous to that in § 10 would then again have enabled us to find a set of values for n and a. But then they would have been less simple than with $v - v_0$. It is easily seen that the result is obtained by substituting $(1+b'_k) : (1-b'_k)$ in $n = (1-x_k) : (x_k - b'_k)$ for unity, and $b'_k : (1-b'_k)$ for b' [1]), so that we then get:

$$n = \left(\frac{1+b'_k}{1-b'_k} - x_k\right) : \left(x_k - \frac{b'_k}{1-b'_k}\right); \quad x_0 = \sqrt[n]{a} = x_k \sqrt[n]{\frac{x_k}{b'_k : (1-b'_k)}},$$

having

$$\frac{b_q - b_0}{b_k - b_0} = \sqrt[n]{\frac{x_k}{x_k - b'_k : (1-b'_k)}}$$

The equation $b = f(v)$ itself becomes:

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

But when we now wish to express n in γ we get, instead of $n = 8\gamma(\gamma+1) : (2\gamma-1)(4\gamma+1)$ according to (31), the less satisfactory expression $(10\gamma+1) : (2\gamma-1)(4\gamma+1)$, in which $10\gamma + 1 = 5b_k + b_0) : b_0$ has a much less simple signification than $8\gamma(\gamma+1) = b_k v_k : b_0^2$. We remind of the fact that x_k is now $= (b_k - b_0) : (v_k - b_k)$, hence $= (2\gamma - 1) : 2$.

And there will be no doubt that more such functions are to be found, which lead to more or less complicated expressions — but we confine ourselves to the above.

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[1]) For where we found above $b'_k = x_k^{n-1} \times (x_k^2 - b'_k x_k) : (a - x_k^n)$, a factor $1 - b'_k$ will now occur by the side of x_k^2, so that after division of both members by $1 - b'_k$ everywhere b'_k has been replaced by $b'_k : (1 - b'_k)$. And in the equation for b''_k, $[b'_k - (b'_k)^2]\, a$ in the first member will be replaced by $(b'_k - (b'_k)^2)(a + x_k^{n+1}) : (1 - b'_k)^2$, when both members are now divided by $(1 - b'_k)^2$. On account of this $b'_k : (1 - b'_k)$ comes everywhere in the second member, where b'_k stood before, while in the first member $(b'_k - (b'_k)^2) \times (a + x_k^{n+1})$, is substituted for $(b'_k - (b'_k)^2)\, a$, the consequence of which is that, after application of entirely the same reductions as above, $nb'_k - 1 - 2nb'_k + (n+1)\, x_k = 0$ is replaced by $nb'_k : (1 - b'_k) - (1 + b'_k) : (1 - b'_k) - 2nb'_k : (1 - b'_k) + (n+1)\, x_k = 0$.

In our concluding paper something will be said about the temperature influence, which will manifest itself by continual diminution of $b_k - b_0$, at first slowly, then more rapidly, as the absolute zero is approached. Descending from high to low temperatures one can therefore pass through all the types. If the critical region of a substance lies in the region of low temperatures, the critical quantities, and also the isotherms in the neighbourhood of the critical point, will present, as far as the course of b is concerned, the little variable type with slight $b_k - b_0$ (γ in the neighbourhood of 0,5). But these same substances will of course show the same variability of b as the "ordinary" substances at high temperatures. Reversely the ordinary substances, considered at low temperatures, will assume the Argon-, Hydrogen- or Helium-type, with respect to the slight variability of b at these temperatures. Etc. Etc.

In this concluding paper I shall also communicate the b-values for Argon I have calculated; besides I shall venture to give some theoretical considerations concerning the diminution of the factor 4 in $b_g = 4m$ with fall of the temperature.

Fontanivent sur Clarens, February 1914.

Mathematics. — "*The envelope of the osculating ellipses, which are described by the representative point of a vibrating mechanism having two degrees of freedom of nearly equal frequencies.*" By H. J. E. BETH. (Communicated by Professor D. J. KORTEWEG).

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

§ 1. In my paper on the small oscillations of mechanisms with two degrees of freedom [1]), LISSAJOUS curves with their envelopes were discussed, which envelopes form the boundaries of the domain of motion. In a summarizing treatment of a more general problem [2]) my further inquiries as to these envelopes have also been included. These inquiries were extended over a system of LISSAJOUS curves, more general than the system which is of importance for the dynamical problem. However the envelopes were considered exclusively from a dynamical point of view, so that purely geometrical properties together with the shape of the curves outside the domain of motion remained unknown. Moreover what came to light about the shape of the envelope remained for the greater part restricted to simple cases, e.g. in the case, formerly indicated by $S = 2$, to the symmetrical case, as quoted, indicated by $p + q = 0$, $l = 0$.

[1]) These Proceedings pp. 619—635 and 735—750 (1910).

[2]) Phil. Mag., sixth series Number 152 (1913).