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Physics. — "*On the value of the critical quantities*". By Prof. Dr. J. D. VAN DER WAALS.

(Communicated in the meeting of March 25, 1911).

Originally by the term *critical quantities* we understood the volume, the pressure, and the temperature of the critical point. For the value of these three quantities $v_k = 3b_g$, $p_k = \frac{1}{27}\frac{a}{b_g^2}$, and $RT_k = \frac{8}{27}\frac{a}{b_g}$ has been derived. But in the determination of these values it has been supposed that the quantity b, which had proved to be variable with the volume, would have changed only so little in the critical point that it might be put equal to the value which it has in infinitely large volume, and which will be denoted by the symbol b_g. But this equation $b_k = b_g$ implied at the same time the neglect of $\left(\frac{db}{dv}\right)_k$ and of $\left(\frac{d^2b}{dv^2}\right)_k$. In course of time the value of other quantities, as they appeared to be in the critical point, have come to the foreground.

In my communication on Quasi association (These Proc. XIII p. 107) I have mentioned $\frac{p_k v_k}{RT_k} = \frac{1}{s}$, $\frac{RT_k}{p_k} = r\,s\,b_g$, $\left(\frac{T}{p}\frac{dp}{dT}\right)_k = f$, $\frac{a}{v_k RT_k} = \frac{f-1}{s}$, and $\left(\frac{v}{v-b}\right)_k = \frac{f}{s}$, which together with the above three quantities $v_k = rb_g$ and $p_k = \frac{a}{b_g^2}\frac{1}{(f-1)r^2}$ and $RT_k = \frac{a}{b_g}\frac{sr}{(f-1)\,r^2}$, forms a number of 8 quantities, which, however. are not independent of each other. If the quantities a and b_g are determined by the choice of the substance, the knowledge of 3 quantities, viz. r, s, and f is sufficient to calculate them all.

From the property of the critical point follows that it is that point of the isothermic line for which the quantities $\left(\frac{dp}{dv}\right)_T$ and $\left(\frac{d^2p}{dv^2}\right)_T$ are equal to 0. So two equations must suffice for the determination. By means of these two equations the quantities v_k and RT_k are determined, and further the value of p_k by means of the equation for p itself. Also the other critical quantities mentioned are then derived by simple mathematical operations. If we put for p:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

the two equations for the determination of v_k and RT_k are:

$$\left(\frac{dp}{dv}\right) = 0 = \frac{RT\left(1-\frac{db}{dv}\right)}{(v-b)^2} - \frac{2a}{v^3} \quad . \quad . \quad . \quad . \qquad \text{(I)}$$

and from the differentiation of 1 and after elimination of RT:

$$\frac{v}{v-b}\left(1-\frac{db}{dv}\right) + \frac{\frac{v}{2}\frac{d^2b}{dv^2}}{1-\frac{db}{dv}} = \frac{3}{2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(II)}$$

If b was known as function of v, II might serve for the determination of v_k, and by means of this I might yield the value of RT_k. If for all substances a same function $\frac{b}{b_g} = f\left(\frac{b_g}{v}\right)$ existed, the same value would always be found for $\frac{b_g}{v_k}$ from II. In other words the quantity r in $v_k = rb_g$ would have the same value for all substances. But then RT_k would be an equally great fraction of $\frac{a}{b_g}$ for all substances, and p_k an equally great fraction of $\frac{a}{b_g^2}$. In the same way $\left(\frac{pv}{RT}\right) = \frac{1}{s}$ would have the same value for all substances — and particularly the investigations of SYDNEY YOUNG show us that great differences exist in the value of s for the different substances. So we are compelled to abandon the assumption that in $\frac{b}{b_g} = f\left(\frac{b_g}{v}\right)$ the course of $\frac{b}{b_g}$ would be the same for all substances. It is clear that this brings the question what may be the cause of the circumstance that b becomes smaller with decreasing volume, to the front again, but for the moment I shall pass over this question in silence. That the value of $r = \frac{v_k}{b_g}$ is smaller than 3, and can be different for the different substances, I shall, however, assume as certain. And in the same way that r descends the more below 3 as b descends more rapidly with v. If we assume a real diminution of the molecule as cause of this variability of b with v, we might put this as follows: the quantity r is the smaller in the critical state as the molecule is the more compressible.

But whatever may be the cause of the variability of b, the law of this change is unknown, and the quantities $\frac{db}{dv}$ and $\frac{v}{2}\frac{d^2b}{dv^2}$, which occur in the equations I and II, are unknown. This excludes the possibility to make these equations serve for a determination of $\frac{v_k}{b_q}$ and of RT_k. Reversely, however, they can serve to determine $\frac{db}{dv}$ and $\frac{v}{2}\frac{d^2b}{dv^2}$ for the critical point, if r and RT_k are known in another way. In consequence of the disappearance of two equations which might serve for the determination of $\frac{v_k}{b_q}$ and RT_k, we must seek two new quantities which might serve us for this purpose, to which the circumstance is added, that now the equality of $b_k = b_q$ also disappears. Hence the knowledge of the 3 quantities r, f, and s is necessary for the determination of the critical data.

I shall assume the equation of p in the simplest form, viz.:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

only with the addition that b depends on v. But I shall assume dependence on T neither of a nor of b. In my investigation, entitled: "Quasi association" it has been demonstrated that such a dependence on T cannot serve to account for the differences with the experiment, but that only the hypothesis of association can effect this. This removes the necessity of the assumption that a and b should be temperature functions. But of course this does not refute the possibility for such a dependence. Here I will investigate, however, in how far the results, obtained on the most simple suppositions, accord with the experiment, and not introduce again an unknown dependence, e.g. of b with T, which would, of course, render the derivation of a definite numerical value, impossible. In my "Quasi association" I have demonstrated that it is probably not of influence for the critical quantities in the shape to which I then reduced them, except for the quantity $\frac{v}{v-b} = \frac{f}{s}$ in a slight degree. The influence of quasi association on the value of the critical quantities being so slight, I shall neglect the quasi association for the sake of simplicity in the derivation of the relations which exist between the critical quantities, either accurate or by approximation. I shall only calculate at the end the extent of the deviations which are the consequence of this association.

Differentiating the equation for p with respect to T, keeping v constant, we find $\left(\frac{dp}{RT}\right)_v = \frac{R}{v-b}$ or $T\left(\frac{dp}{RT}\right)_v = \frac{RT}{v-b} = p + \frac{a}{v^2}$; and as

$\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{kr}$ in the critical point, we get:

$$T\left(\frac{dp}{dT}\right)_{kr} - p = \frac{a}{v^2}.$$

In this last equation $\left(\frac{dp}{dT}\right)_{kr}$ represents the increase of tension of the saturate vapour, as it is at the critical temperature. We may also write:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_{kr} - 1 = \frac{a}{p_k v_k^2}$$

or

$$p_k = \frac{a}{v_k^2\left[\frac{T}{p}\frac{dT}{dp} - 1\right]_{kr}}.$$

And putting $v_k = rb_g$

$$p_k = \frac{a}{b_g^2}\frac{1}{r^2\left[\frac{T}{p}\frac{dp}{dT} - 1\right]_{kr}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

For a number of substances the tension of the saturate vapour has been experimentally determined up to T_k — and especially the values of p for some thirty substances have been given by SYDNEY YOUNG in "The Scientific Proceedings of the Royal Dublin Society" (June 1910). These tensions have been determined for temperatures between T_k and about $\frac{1}{2}$ T_k.

By approximation they are indicated by the empirical formula:

$$-Nep\ log\frac{p}{p_k} = f\frac{T_k - T}{T}$$

or

$$-Nep\ log\ \pi = f\frac{1-m}{m}.$$

But the quantity f is somewhat variable with m; starting from T_k or $m = 1$ there seems to be at first some diminution of f with descending value of m, which, however, has already been replaced by a rise for $m < \frac{1}{2}$, while for $m = \frac{1}{2}$ the value of m has again risen above f_k. For still smaller value of m the observation is prevented by the appearance of the solid state. From some phenomena I have concluded as probable that e.g. at $f_k = 7$ the limiting value of f would rise to about 9 at the absolute zero.

From this empirical formula we derive:

$$-\frac{d\pi}{\pi dm} = -\frac{f_m}{m^2} + \frac{1-m}{m}\frac{df_m}{dm}$$

or

$$\frac{md\pi}{\pi dm} = \frac{f_m}{m} - (1-m)\frac{df_m}{dm},$$

and so

$$\left(\frac{m}{\pi}\frac{d\pi}{dm}\right)_{k_r} = f_k$$

If we wish to determine the value of f_k perfectly accurately, we are confronted, even with SYDNEY YOUNG's determinations, by difficulties. SYDNEY YOUNG represents the form of p by the formula of BIOT, viz. $Log\, p = a + ba^T + c\beta^t$; on the whole he succeeds in determining the many constants occurring in the formula so that the agreement with the experimental data is very satisfactory. But though we confine ourselves to the socalled normal substances — so excluding acetic acid and the alcohols — yet appreciable differences occur, especially in the neighbourhood of T_k. Differences great enough to be of importance for the value of $\left(\frac{md\pi}{\pi dm}\right)_{kr}$ which is to be calculated. A very elaborate investigation would be required to determine the most probable value of f_k. And perhaps the most reliable method for the calculation of this quantity is the direct one; viz. by reading as well $d\pi$ as dm and π and m at temperatures near T_k from the table of the observations. As an example I calculate for ethyl-acetate from:

p	T
26740	245
27535	247
28370	249
28800	250
28877	250,1

From the two first observations follows for $\frac{Tdp}{pdT}$ or $\frac{md\pi}{\pi dm}$ the value $\frac{795 \times 519}{27137 \times 2} = 7{,}6$. From the 3rd and 4th observation $\frac{430 \times 522{,}5}{28585} = 7{,}86$, while the difference of the temperatures is too slight for the calculation from the two last observations. The rise of p, which per degree is equal to 395 at $T=246$, and to 430 at $T=249{,}5$, would namely suddenly be equal to 770 at 250,05. Thus much we shall no doubt be able to conclude that f_k will not differ much from 7,6 or 7,8 for ethyl-acetate. I have thought I ought to call attention to this uncertainty of the absolutely accurate value of f_k, as we shall presently subject a probable relation between the values of some critical quantities to an investigation.

Let us now proceed to derive a value for RT_k. We do this by the aid of the value of what is often called "critical coefficient", which is also to be derived from the determinations of SYDNEY YOUNG and given by himself; viz. the quantity s from the relation:

$$\frac{RT_k}{p_k v_k} = s.$$

The uncertainty which exists in this quantity s is for the greater part the consequence of the uncertainty in the value of v_k. In most cases v_k was not directly determined, but calculated from the course of the value of liquid- and vapour volume at temperatures near T_k. This can be done with the aid of the law of the rectilinear diameter, or by applying the criterion $\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{kr}$. For RT_k we find now the value:

$$RT_k = \frac{a}{b_g} \frac{sr}{(f_k - 1)r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Eliminating b_g and r, we find from equations (I) and (II):

$$\frac{(RT_k)^2}{p_k} = a \frac{s^2}{f-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

In my Quasi-association (These Proc. June 1910) I pronounced the expectation that at least approximately the factor of a, viz. $\frac{s^2}{f-1}$ would always have the same value for all normal substances, whatever might be the law of variability for the quantity b. I have since been strengthened in this opinion by the investigation of the value of $\frac{s^2}{f-1}$ for all normal substances, for which the quantities s and f have been determined experimentally.

If b does not vary with v, the value of $\frac{s^2}{f-1}$ is equal to $\frac{64}{27}$, and so we have to examine if $\frac{s^2}{f-1}$ is always found equal to this value.

In order to investigate the correctness or incorrectness of this relation as impartially as possible, I have taken the values for s and f which are given by KUENEN (Die Zustandsgleichung etc.), and then calculated s from:

$$s = \sqrt{\frac{64}{27}(f-1)}$$

and compared this value with the given one. The values of f occur on p. 142 and those for s on p. 60. KUENEN's numerical values, however, have been chosen so as to belong to the equation:

$$-\log_{10} \pi = f' \frac{1-m}{m}$$

and so to yield the values of f meant in the formula $\frac{s^2}{f-1} = \frac{64}{27}$ KUENEN's values must be divided by 0,4343.

	f'	f	s calculated	s given	
H_2	2.10	4.835	3.01	2.94	(?)[1]
Argon	2.18	5.02	3.08	2.67	
O_2	2.50	5.757	3.36	3.49	(?)
Ethylene	2.75	6.33	3.55	3.42	
CO_2	2 86	6.58	3.636	3.59	
Ethane	2.60	6	3.443	3.55	
CCl_4	2.81	6.47	3.606	3.67	
Benzene	2.89	6.65	3.67	3.75	
Fluor-benzene	2.99	6.885	3.735	3.78	
Ether	3.01	6.93	3.75	3.81	
Esters	2.97—3.25	6.84—7.48	3.715—3.92	3.86—3.94	

First of all in this table the great difference in calculated and given value of s for Argon is very striking — and this led me to inquire into the cause for this great difference. Now before the appearance of the Proceedings of the Royal Society of Febr. 1911 I happened to look through the proof, and in this way I got acquainted with the observations of KAMERLINGH ONNES and CROMMELIN, who give values for f' and s for Argon. There the value 3,283 is given for s, so still greater than in KUENEN's list. But on the other hand f' is much greater than is given above. If we take the value of f' at $t = -125{,}49$, viz. 2.577, then $f = 5.934$, and we calculate $s = 3.41$; -- again appreciably greater than 3,283. This led me to calculate the value of f_k itself from the data occurring in the cited communication. Specially because a sudden increase takes place in the given value of f' near the critical temperature, which is not the case for other substances to the same extent. Between $t = -140.80$ and $t = -125.49$ KAMERLINGH ONNES and CROMMELIN give four values for f' for ascending temperatures, viz. 2.415, 2.421, 2.457, and finally 2.577. The last value I have re-calculated — and I come

[1]) The (?) mark is KUENEN's.

to the conclusion that it is too large. In two ways I have tried to determine f' and so also f. First of all by taking Δp, ΔT and p and T between the two highest temperatures, and substituting into the formula $f = \frac{T\Delta p}{p\Delta T}$. We find $\Delta p = 6.611$, $\Delta T = 4.34$, $p = 39{,}1515$ and $T = 145.34$ and from this $f = 5.66$ — and in the second place by calculating f' from $-\log_{10}\frac{p}{p_k} = f'\frac{T_k - T}{T}$. Then we find $f' = 2.425$ and $f = 5.6$. So the sudden increase in the value of f' does not exist. With $f = 5.6$ we calculate $s = 3.29$ — which lies exceedingly near the value 3.283 found.

So in this case we have an almost perfect harmony between the formula which supposes $\frac{s^2}{f-1} = \frac{64}{27}$, and the observation for a substance with very low critical temperature. For one with a high value of s, viz. ethyl-acetate, for which $s = 3.949$ is put by SYDNEY YOUNG, we get as good an agreement if we put f between 7.6 and 7.8, as was found above (p. 1215). With $f = 7.7$ we find $s = 3.977$, while SYDNEY YOUNG gives $s = 3.949$.

Only for helium a very great divergence would be found. In the paper already mentioned in the discussion of Argon $s = \frac{8}{3}$ is put for helium. To this corresponds $f = 4$ or $f' = 1.7372$ — while $f' = 1.2$ is given as highest value. But then $f = 4$ is the lowest value for f, which is possible according to the equation of state — unless we should accept the perfectly inconceivable supposition that b increases with v.

If we examine the validity of the relation $\frac{s^2}{f-1} = \frac{64}{27} = 2.37$ for the alcohols and acetic acid according to the observations of SYDNEY YOUNG, we are in the first place struck with the difficulty to derive the value of f_k with any certainty from the observations. For methyl-alcohol there is at the higher temperatures generally a great difference between the observations and the formula of BIOT used by SYDNEY YOUNG — differences which irregularly change their signs at temperatures which differ only 1 or $^1/_2$ degree. As probable value of f_k I have chosen 8.35. If the said relation between s and f existed, $s = 4.17$ would correspond to this, while SYDNEY YOUNG gives $s = 4.559$. For methyl-alcohol the same difficulty in the determination of f_k holds, for this substance I think I have to assume the value 8.5. According to the above relation $s = 4.215$ would correspond to this, while SYDNEY YOUNG gives the value 4.26 for s. For propylalcohol I have chosen f_k equal to 7.78, which differs greatly from KUENEN's value 3.93. The value thought probable by me agrees almost entirely with 3.39 instead with 3,93. According to the above relation $s = 4$ corresponds to it, while SYDNEY YOUNG gives $s = 3{,}998$. So tested by the above relation propyl-alcohol would already be a normal substance. But for acetic acid, for which at low temperatures the saturate vapour already consists almost entirely of double molecules, the relation does not hold at all.

If it is taken into consideration that the values of f, printed unmodified in the above table are mean values, which may only accidentally be the values of f_k — I feel justified in assuming that for normal substances $\frac{s^2}{f-1} = \frac{64}{27}$ may be considered as valid at least to a high degree of approximation. Accordingly I harbour the expectation that further investigation will make the exception for helium disappear. If, however, this small value of f is found confirmed on further investigation, helium would have to be called a very abnormal substance.

So the quantity a is determined from T_k and p_k by the relations already given in my Thesis for the doctorate, at least to a high degree of approximation.

In my Quasi-association I had arrived at this relation through the assumption that in the critical point two quantities would have the same values as follows from the assumption $b =$ constant, viz. $sr = 8$ and $(f-1)\,r^2 = 27$. Then $s^2r^2 = 64$ and after elimination of r we get the equation $\frac{s^2}{f-1} = \frac{64}{27}$. But the equation obtained after elimination of r can be valid without sr and $(f-1)\,r^2$ being constant. Thus e.g. with $sr = 7{,}5$ and $(f-1)\,r^2 = 23{,}34$ the same relation between s and f can be refound. So the question is now whether both relations ($sr = 8$ and $(f-1)\,r^2 = 27$) may be considered as valid to a high degree of approximation. As v_k could indeed be determined experimentally, but not $r = \frac{v_k}{b_g}$, I had arrived at the supposition $sr = 8$ and $(f-1)\,r^2 = 27$, by assuming a value for r which could not be far from the correct one.

I have tried to determine what would follow for different properties of the quantities in the critical point if the two relations men-

80*

tioned should be perfectly accurate, viz. 1. For the quantity $\frac{b_k}{bg}$, 2 the quantity $\left(\frac{db}{dv}\right)_k$, and 3 the quantity $\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_k$.

1. The quantity $\frac{b_k}{bg}$ is found by determining $\left(T\frac{dp}{dT}\right)_k$: equal to $f_k = \frac{1}{p}\frac{RT}{(v-b)_k}$, or $\frac{f}{s} = \frac{v}{(v-b)_k} = \frac{r}{r - \frac{b_k}{bg}}$, from which follows:

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

With $rs = 8$, we should find:

$$\frac{b}{bg} = r - \frac{8}{f}.$$

I shall, however, not at once suppose $rs = 8$, nor $(f-1)r^2 = 27$, but assume $rs = c_1$, and $(f-1)r^2 = c_2$, and c_1 and c_2 to be variable with r. Differentiating the relation:

$$\frac{b}{bg} = r - \frac{rs}{f} = r - \frac{c_1}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

with respect to r we get, because bg does not depend on r:

$$\frac{db}{bgdr} = 1 + \frac{c_1}{f^2}\frac{df}{dr} - \frac{1}{f}\frac{dc_1}{dr}$$

or

$$\frac{db_k}{dv_k} = 1 + \frac{c_1}{f^2}\frac{df}{dr} - \frac{1}{f}\frac{dc_1}{dr}$$

From $(f-1)r^2 = c_2$ follows $\frac{1}{f-1}\frac{df}{dr} + \frac{2}{r} = \frac{dc_2}{c_2dr}$, in consequence of which we get:

$$\frac{db_k}{dv_k} = 1 - \frac{2s(f-1)}{f^2} + \frac{c_1(f-1)}{f^2}\frac{dc_2}{c_2dr} - \frac{1}{f}\frac{dc_1}{dr}.$$

And by means of the relation $\frac{c_1^{\,2}}{c_2} = \frac{s^2}{f-1}$ = constant, or

$$2\frac{dc_1}{c_1} = \frac{dc_2}{c_2}$$

finally:

$$\frac{db_k}{dv_k} = 1 - \frac{2s(f-1)}{f^2} + \frac{dc_1}{dr}\frac{f-2}{f^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

The equation (IV) gives us the fraction which in the critical point is the quantity b of bg. It appears, as was to be expected, to be dependent on the value of r for this point. If rs should always be equal to 8, and $(f-1)\,r^2 = 27$, this fraction would be determined by r and depend on it in the following way:

$$\frac{b}{bg} = r - \frac{8}{1 + \frac{27}{r^2}}.$$

For $r = 3$, the greatest value which r can assume, we find $\frac{b}{bg} = 1$, as was to be expected. But though this quantity decreases with the decrease of r, as was to be expected, this decrease is slight; thus with $r = 2$ the value of $\frac{b}{bg} = \frac{30}{31}$.

Equation (V), derived from (IV), reveals the direction of the tangent to the locus (IV), and for the case that sr would always be equal to 8, it yields for $\frac{d\left(\frac{b}{bg}\right)}{dr}$ the value:

$$1 - \frac{2s\,(f-1)}{f^2}$$

which for $s = \frac{8}{3}$ and $f = 4$ is equal to 0, for $s = 3{,}77$ and $f = 7$ to $\frac{3.76}{49}$, and for $s = 4$ and $f = \frac{31}{4}$ to $\frac{97}{961}$.

2. The quantity $\left(\frac{db}{dv}\right)_{k}$. This quantity is found from the condition that $\left(\frac{dp}{dv}\right)_T$ must be equal to 0 in the critical point.

From $\left(\frac{dp}{dv}\right)_T = 0$, we find:

$$\frac{RT\left(1 - \frac{db}{dv}\right)}{(v-b)^2} = \frac{2a}{v^3}$$

or

$$1 - \left(\frac{db}{dv}\right)_{kr} = \frac{2a}{v_k RT_k}\left(\frac{v-b}{v}\right)^2_{k}.$$

And substituting the value $\frac{a}{v_k RT_k} = \frac{f-1}{s}$ and $\left(\frac{v-b}{v}\right)_{k} = \frac{s}{f}$, in it, which values already occur in my paper on quasi association, we find:

$$1-\left(\frac{db}{dv}\right)=\frac{2s\,(f-1)}{f^2}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VI)$$

Comparing this value with (V) we see that if c_1 should be independent of r, and so $c_1 = sr$ always strictly equal to 8, the value of $\left(\frac{db}{dv}\right)_{kr}$ would be perfectly the same as $\frac{db_k}{dv_k}$. But these two quantities do not mean the same thing. The meaning of what I have represented by $\left(\frac{db}{dv}\right)_{kr}$ is clear. We have a substance with definite a and b_q. The quantity b, which is only equal to b_q for infinitely large volume, decreases on decrease of the volume, whatever may be its cause and the law according to which it decreases. Starting from very large volume, the decrease is so small at first that it can practically be neglected, and $\frac{db}{dv}$ may be put almost equal to 0. I have represented the value which $\frac{db}{dv}$ has in the critical point, by $\left(\frac{db}{dv}\right)_{kr}$.

The way in which, even for substances with the same value of b_q, the quantity b depends on v appears to be different, and this circumstance calls up the question again, what is, after all, the cause of this variability of b. At the critical point $\frac{b}{b_g}$, $\frac{db}{dv}$, and as we shall more fully discuss later on $\frac{d^2b}{dv^2}$, are very different. And the different way in which b depends on v, is the cause, that the quantities s, f and r differ in the critical point.

But the significance of $\frac{d\left(\frac{b}{b_g}\right)}{dr}$, which quantity I have represented in (V) by $\frac{db_k}{dv_k}$, is another. The equation (IV), from which it has been derived, viz. $\frac{b_k}{b_g}=r-\frac{c_1}{f}=r\left(1-\frac{s}{f}\right)$ enables us to calculate $\frac{b}{b_g}$ in the critical point, when r, s and f should be known for a substance, and may therefore be considered as a locus holding for all substances, whatever may be the law of dependence of b with v.

So it does not belong to a single substance. If the dependence of b with v is given, only a single point of this locus refers to this substance, viz. that point in which $\frac{b}{b_g}=f(v)$ for that definite substance intersects the locus. And if we knew this locus perfectly, and also the value of $\frac{b}{b_g}$ for that definite substance, we could determine the critical point by determining where $\frac{b}{b_g}$ intersects the given locus For greater values of r the curve $\frac{b}{b_g}$ for the definite substance lies below the locus, and for smaller value of r above it. And it follows already from this that $\left(\frac{db}{dv}\right)_{kr}$ must be smaller than $\frac{db_k}{dv_k}$, or $1-\left(\frac{db}{dv}\right)_{kr} > 1-\frac{db_k}{dv_k}$.

Then it follows by comparison of (V) with (VI) that $\frac{dc_1}{dr}$ must be positive. This means that sr is equal to 8 only for $r=3$, or for constant value of b; but in all other cases, so if b decreases with v, it is smaller than 8, and the more so as the variability of b is stronger.

Now the value of the factor of $\frac{a}{b_g}$ for RT_k does not only depend on sr. This factor is $\frac{rs}{(f\ \ 1)r^2}$ or $\frac{c_1}{c_2}$. Representing this factor by F, we get $\frac{dF}{Fdr}=\frac{dc_1}{c_1dr}-\frac{dc_2}{c_2dr}$. And $\frac{c_1{}^2}{c_2}$ being constant, $2\frac{dc_1}{c_1dr}=\frac{dc_2}{c_2dr}$. Hence $\frac{dF}{Fdr}=-\frac{dc_1}{c_1dr}$. To find this result, we might also have written the factor of $\frac{a}{b_g}$: $\frac{(rs)^2}{(f-1)r^2}\frac{1}{rs}$ or $\frac{64}{27}\frac{1}{rs}$. So if for all substances for which b is variable with v $rs<8$, then $RT_k>\frac{8}{27}\frac{a}{b_g}$ and this result might also have been arrived at in a simpler way.

Let us imagine for this purpose two substances with given a and b_g — the former with constant b, the latter with b decreasing with diminishing v. If for given value of T we plot an isotherm for both substances — we see at once that the isotherm for the second substance will always lie below that of the first substance. As for every value of v the quantity $v—b$ is greater for the second substance than for the first, $\frac{RT}{v-b}$ is smaller for the first substance than for the second, and $\frac{a}{v^2}$ being the same for the two substances, $p_2<p_1$. For

great volumes b for the second substance is only very slightly smaller than b_g, and for great volumes the two isotherms may almost be considered as coinciding. But still, the fact remains that there is a difference, and that this difference increases with decrease of volume, and that this difference is the greater as the variability of b is more pronounced.

At a value of v, for which $\frac{dp}{dv}=0$ in the isotherm which lies above the other, $\frac{dp}{dv}$ is positive in the lower isotherm. So the limits for the unstable region are further apart in this case than for the upper isotherm. But the displacement of these limits is more considerable on the side of the small volumes. At the critical temperature of the first substance, so at $RT_k=\frac{8}{27}\frac{b}{bg}$, $\frac{dp}{dv}$ will still be positive for $v=3bg$ for the second substance, and so the temperatures will still have to rise, and become greater than $\frac{8}{27}\frac{a}{bg}$, before the critical temperature of the second substance is reached.

But though we know that sr is smaller than 8 in all cases in which b becomes smaller at the same time with v, and the more so as b varies more rapidly with v, still we have no rule as yet to determine the value of this quantity. Of course, this would be the case, if the law of the variability of b was known.

For instance, if $\frac{b}{bg}=1-\alpha\frac{bg}{v}$ could be put, which might be done for not too small volumes, if the reason of the variability of b is not a real diminution of the molecule, but must be ascribed to an apparent diminution, as I already did in 1873. Then (IV) reduces to:

$$1-\frac{\alpha}{r}=r-\frac{rs}{f}$$

and (VI) to:

$$1-\frac{\alpha}{r^2}=\frac{2s(f-1)}{f^2}$$

and with elimination of α, the approximate equations to:

$$1-\frac{1}{r}=\frac{2s(f-1)}{f^2}-1+\frac{s}{f}$$

or

$$\frac{1}{r}=2-\frac{3s}{f}+\frac{2s}{f^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (VII)$$

or

$$\frac{1}{sr}=\frac{2}{s}-\frac{3f-2}{f^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (VIII)$$

For $s=\frac{8}{3}$ and $f=4$, we find of course again $sr=8$, but to this a value of $\alpha=0$ belongs. With $s=3{,}64$ and $f=6{,}6$ we find for CO_2 the value $sr=7{,}1$, which value is smaller than I had expected. For ether, for which we may put $s=3{,}77$ and $f=7$, we find sr little different from 7,1. Small errors in v and f, however, have a great influence on the value of this quantity. For r a value is found little higher than 1,88. That in my "Quasi association" I put sr little different from 8 also for substances like ether is, therefore owing to a too high value for r. If the value of α is calculated from $1-\frac{\alpha}{r}=r-\frac{rs}{f}$ or from $1-\frac{\alpha}{r^2}=\frac{2s\,(f-1)}{f^2}$, α is found to differ little from $^3/_8$. This result would be in perfect accordance with what the theory had predicted concerning the value of α in the approximate formula used for spherical molecules. But we find another value of α for another value of s and f.

The relation between α and f is given by the formula:

$$\alpha\frac{1}{r^2}=1-\frac{2s\,(f-1)}{f^2}$$

and by the aid of (VII)

$$\alpha\left\{2-s\,\frac{3f-2}{f^2}\right\}^2=1-\frac{2s\,(f-1)}{f^2}$$

from which we derive:

$$\frac{f^2}{s}\,\frac{d\alpha}{df}=(f-2)\frac{-\frac{1}{f-1}+\frac{s}{f^2}\left(3-\frac{4}{f^2}\right)}{\left(2-s\,\frac{3f-2}{f^2}\right)^3}$$

This value of $\frac{d\alpha}{df}$ is equal to 0 for $f=4$ and $s=\frac{8}{3}$, but for greater value of f and corresponding value of s it is always positive, as, indeed, might have been expected. It was, namely, to different variability of b with v that we attributed the different value of f and s. But the different value of α is still inexplicable. Is the deviation from the spherical shape the cause? And is, for the cases in which $\alpha>\frac{3}{8}$, another cause, a real diminution of the molecule added to the cause assumed up to now for the decrease of b? But the assumption :

$$\frac{b}{b_g} = 1 - \alpha \frac{b_g}{v}$$

becomes altogether improbable by the consideration of the value of $\frac{d^2b}{dv^2}$.

3. The quantity $\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr}$. This quantity is found from the condition that $\left(\frac{d^2p}{dv^2}\right)_T$ is $=0$ in the critical point.

Equation (II):

$$\frac{v}{v-b}\left(1-\frac{db}{dv}\right) + \frac{\frac{v}{2}\frac{d^2b}{dv^2}}{1-\frac{db}{dv}} = \frac{3}{2}$$

yields for the value of $\frac{v}{2}\frac{d^2b}{dv^2}$, if we put $\frac{v}{v-b} = \frac{f}{s}$ and $\left(1-\frac{db}{dv}\right) = \frac{2s(f-1)}{f^2}$:

$$-\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr} = \frac{s(f-1)(f-4)}{f^3} \quad . \quad . \quad . \quad . \quad . \quad (IX)$$

For $f=4$ we find this value again equal to 0. For $f=7$ and $s=3.78$ the value is equal to $0.54 \times \frac{18}{49}$ or nearly 0,2.

The equation (IX) can be derived from (VI) without it being necessary to have recourse to (II). Nor need (VI) be derived from (I). From the relation $\frac{b}{bg} = r - \frac{rs}{f}$ we could have found $\left(\frac{db}{dv}\right)_{kr}$ from v by keeping c_1 constant as should be done for a constant substance. Then we get:

$$1 - \frac{db}{dv} = \frac{2s(f-1)}{f^2}$$

and by differentiation of this equation, keeping c_2 constant:

$$-\frac{d^2b}{dv^2}dv = 2ds\frac{f-1}{f^2} + 2s\left(-\frac{1}{f^2}+\frac{2}{f^3}\right)df$$

or

$$-\left(v\frac{d^2b}{dv^2}\right)\frac{dv}{v} = \frac{s}{f^2}\left\{2\frac{ds}{s}(f-1) + 2\left(-1+\frac{2}{f}\right)d\right\}.$$

Writing $\frac{dr}{r}$ for $\frac{dv}{v}$, and df for $2\frac{ds}{s}(f-1)$, we find:

$$-\left(\frac{vd^2b}{dv^2}\right)_{kr}=\frac{r\,df}{dr}\frac{s}{f^2}\left\{1-2+\frac{4}{f}\right\}=\frac{rdf}{dr}\frac{s}{f^3}(-f+4),$$

and as $\dfrac{df}{f-1}+\dfrac{2dr}{r}=0$:

$$-\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr}=\frac{s(f-1)(f-4)}{f^3},$$

and

$$-\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr}=\frac{f-4}{2f}\left(1-\frac{db}{dv}\right)_{kr}.$$

As $\left(1-\dfrac{db}{dv}\right)_{kr}$ differs little from 1, we have in $\dfrac{f-4}{2f}$ an approximate value for $-\left(\dfrac{v}{2}\dfrac{d^2v}{db^2}\right)_{kr}$.

The value of $-\left(\dfrac{v}{2}\dfrac{d^2b}{dv^2}\right)_{kr}$ is exceedingly great, in comparison with $\left(\dfrac{db}{dv}\right)_{kr}$, and this latter is again great in comparison with $1-\dfrac{b}{b_g}$. And that this could not be accounted for, if we put $\dfrac{b}{b_g}=1-\alpha\dfrac{b_g}{v}$, is particularly obvious if we compare $-\left(\dfrac{v}{2}\dfrac{d^2b}{dv^2}\right)_{kr}$ with $\left(\dfrac{db}{dv}\right)_{kr}$. Putting $\dfrac{b}{b_g}=1-\alpha\dfrac{b_g}{v}$, we find then $\left(\dfrac{db}{dv}\right)=\alpha\left(\dfrac{bg}{v}\right)^2$, and in the same way $\left(-\dfrac{v}{2}\dfrac{d^2b}{dv^2}\right)=\alpha\left(\dfrac{bg}{v}\right)^2$. The ratio of the two mentioned values would then be 1.

We might account for the high ratio between the two quantities by an equation of the following form:

$$\frac{b}{bg}=1-\alpha\left(\frac{bg}{v}\right)^n$$

Then $\dfrac{db}{dv}=n\alpha\left(\dfrac{b_g}{v}\right)^{n+1}$ and $\left(-\dfrac{v}{2}\dfrac{d^2b}{dv^2}\right)=\dfrac{n(n+1)\alpha}{2}\left(\dfrac{bg}{v}\right)^{n+1}$, so that the ratio would be $\dfrac{n+1}{2}$. Then for the determination of n we have the equation:

$$\frac{n+1}{2}=\frac{\dfrac{s(f-1)(f-4)}{f^3}}{1-\dfrac{2s(f-1)}{f^2}}.$$

For $n = 4$ and $s = \frac{8}{3}$ numerator and denominator are equal to 0, but this case supposes $b = b_q$. For $s = 3.78$ and $f = 7$ we should find:

$$n + 1 = \frac{1.08 \times \frac{6}{7} \times \frac{3}{7}}{1 - 1.08 \times \frac{6}{7}} = 5.34$$

or

$$n = 4.34$$

For the determination of r we have the equations:

$$\frac{b}{bg}\frac{1}{r} = 1 - \frac{s}{f}$$

or

$$\frac{1 - \frac{a}{r^n}}{r} = 1 - \frac{s}{f}$$

or

$$\frac{1}{r} = 1 - \frac{s}{f} + \frac{a}{r^{n+1}} = 1 - \frac{s}{f} + \frac{\frac{db}{dv}}{n}$$

or

$$\frac{1}{r} = 1 - \frac{s}{f} + \frac{1 - \frac{2s(f-1)}{f^2}}{n}$$

For $s = 3.78$ and $f = 7$ and $n = 4.34$, we find:

$$\frac{1}{r} = 0{,}46 + 0{,}01713 = 0\ 47713$$

or

$$r = 2{,}0957.$$

And this value of r is, indeed, smaller than the estimation in my "Quasi association", but only very little.

On the supposition that sr should always be equal to 8, we should find $r = 2{,}116$ — so that the difference would hardly amount to 1 %. Hence we find $sr < 8$, as was demonstrated above, but only little smaller, viz. 7,9217. And for $(f-1)r^2$ we do not find exactly 27, but a slightly smaller value, viz. 26,352. But the question what is, after all, the cause of the variability of b, is not answered yet, and

$\frac{b}{b_q} = 1 - \alpha \left(\frac{b_q}{v}\right)^n$ is to be considered only as an empirical formula, holding by approximation in the neighbourhood of v_k.

Now, however, it remains to investigate in how far the existence of Quasi association has influence on the obtained results.

In general:

$$\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{vx} + \left(\frac{dp}{dx}\right)_{vT} \left(\frac{dx}{dT}\right)_v.$$

And $\left(\frac{dp}{dT}\right)_v$ being equal to $\frac{dp}{dT}$ in the critical point, also:

$$T\frac{dp}{dT} = \frac{RT\left\{1 - \frac{n-1}{n}x\right\}}{v-b} + \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v$$

or

$$T\frac{dp}{dT} - p = \frac{a\left(1 - \frac{x}{2}\right)^2}{v^2} + \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v.$$

Now we have chosen the quantity n so, that:

$$T\frac{dp}{dT} - p = \frac{a}{v^2}$$

or in such a way that:

$$\frac{a\left(x - \frac{x^2}{4}\right)}{v^2} = \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Now the value of $\left(\frac{dx}{dT}\right)_v$ is necessarily negative, and so the value of $\left(\frac{dp}{dx}\right)_{vT}$ will also be negative for the chosen value of n.

Though the ψ-surface has minimum value of T_k for a definite value of x, a section at given value of v will not begin with increase of p, as is usually the case; but will always show decreasing value of p. The value of $\left(T\frac{dx}{dT}\right)_v$ we must determine by differentiation of $\left(\frac{d\psi}{dx}\right)_{vT} = 0$ and so from the equation:

$$\left(\frac{d^2\psi}{dx\,dv}\right)_T dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx + \left(\frac{d^2\psi}{dx\,dT}\right)_v dT = 0$$

or

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\eta}{dx}\right)_{vT} dT = 0$$

or

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\varepsilon}{dx}\right)_{vT} \frac{dT}{T}$$

And as $\varepsilon = -Ex - \dfrac{a\left(1-\dfrac{x}{2}\right)^2}{v}$

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx + \left[E - \frac{a\left(1-\dfrac{x}{2}\right)}{v}\right]\frac{dT}{T} = 0$$

From this we find:

$$T\left(\frac{dx}{dT}\right)_v = -\frac{E - \dfrac{a\left(1-\dfrac{x}{2}\right)}{v}}{\left(\dfrac{d^2\psi}{dx^2}\right)_{vT}}.$$

The value of $\left(\dfrac{d^2\psi}{dx^2}\right)_{vT}$ I gave (These Proc. June 1910) in the form:

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} = RT\left\{\frac{1+(n-1)x}{nx(1-x)} - \frac{a}{2vRT}\right\}$$

But there has an error slipped in there, which is indeed without influence for small value of x, but which I must yet rectify. As this would here divert us from the question we are dealing with, I shall discuss the way in which the rectification is obtained, later on, and now only give the corrected value. We should find:

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} = RT\left\{\frac{1}{nn(1-x)\left(1-\dfrac{n-1}{n}x\right)} - \frac{a}{2vRT}\right\}$$

Substituting the value of $\left(T\dfrac{dx}{dT}\right)_v$ in equation (α) we find with a high degree of approximation (for small value of x):

$$1 = -v\left(\frac{dp}{dx}\right)_{vT} \frac{\left(E\dfrac{vk}{a} - 1\right)}{RT} n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

If we write the value of p in the following form:

$$p+\frac{a}{v^2}=\frac{RT\left(1-\frac{n-1}{n}\right)}{v-b}+\frac{a\left(x-\frac{x^2}{4}\right)}{v^2}$$

Bearing in mind that $p+\frac{a}{v^2}=T\frac{dp}{dT}$, we find for small value of x:

$$T\frac{dp}{dT}=\frac{RT}{v-b}+x\left(\frac{dp}{dx}\right)_{vT}$$

according to (β)

$$T\frac{dp}{dT}=\frac{RT}{v-b}-\frac{xRT}{v}\frac{1}{n\left(\frac{Ev_k}{a}-1\right)}$$

or dividing by p:

$$f=s\frac{v}{v-b}-s\frac{x}{n\left(\frac{Ev_k}{a}-1\right)}$$

So the value of $\frac{v}{v-b}$ is found to be somewhat greater than $\frac{f}{s}$, but so little that our foregoing calculations can remain unchanged.

Geophysics. — *"On tidal forces as determined by means of* WIECHERT'S *astatic seismograph"*. By Dr. C. BRAAK. (Communicated by Dr. VAN DER STOK.)

(Communicated in the meeting of March 25, 1911).

In a previous communication the E—W component of the semi-diurnal lunar tidal motion of the ground at Batavia, as deduced from registrations of WIECHERT'S astatic seismograph during the period of July to December 1909, was stated to be:

$$0''.0114 \cos(2t-251°\ 53)^{1)},$$

whereas the theoretical value is:

$$0''.0155 \cos(2t-270°)$$

The registrations obtained during the following half-year have now been worked out upon the same plan and, in addition to this tide, the other principal tides have been calculated for the whole period of one year, except the semi-diurnal solar tide, which is strongly disturbed by the diurnal heat wave.

These tides, enumerated according to their importance, are:

1) These Proceedings XIII. 1910, p. 17—21.