Citation:

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temperature (with a view to determining which the experiments of KAMERLINGH ONNES and PERRIER were undertaken (see Comm. N°. 116 § 1) would be given by a series of similar lines, differing for the different densities.

We must not forget that it is by no means established that in the case of oxygen the divergence from CURIE's law is determined by a Δ' which changes with the density, and that it obviously may be due to an association of molecules into complexes with a diminution of the number of magnetons.

However this may be, our attention is again drawn to the important question whether the divergences from CURIE's law depend upon a peculiarity of the atom within the single molecule or from the approach of the molecules up to a very small distance.

In § 3 of Comm. N°. 122*a* by KAMERLINGH ONNES and PERRIER, it is said that preliminary experiments with mixtures of liquid oxygen and nitrogen, which will soon be replaced by better final ones and which were based on the above mentioned association hypothesis, seemed to indicate that bringing the molecules to a greater distance by dilution in the liquid state has no influence of importance upon the divergences from CURIE's law. Here the question is raised in this form: whether Δ' is a quantity which as peculiar to the atom in the single molecule can also be found in the gaseous state or whether it can only be developed by bringing the molecules into immediate vicinity of each other. Further experiments [1]) with oxygen, already planned, must decide this.

(*To be continued*).

Physics. — "*The law of corresponding states for different substances.*" By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of December 28, 1912).

In the following pages I shall give an account of the result of the researches which I have made of late about the properties of the equations of state for different substances. And I shall communicate in them the simple conclusion at which I have arrived for all the substances for which a chemical combination does not take place, and the molecules continue to move separately, either really isolated, or perhaps joined to groups, if this aggregation (quasi association) behaves in the same way.

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[1]) As this communication is going to press, these experiments have advanced so far, that we may accept with great probability as the result of them, that gaseous oxygen of 90 times the normal density obeys CURIE's law down to — 130° C.

When I discovered the law of corresponding states, I could state the result in two way — and in the beginning I, therefore, hesitated before making a choice between these two ways of expression: 1. if for the different substances π and m are equal, $\nu = \frac{v}{v_{k_n}}$ is also equal, 2. if for the different substances π and m are equal, the volume for all is the same number of times the volume of the molecules. For so far as I saw then these two expressions were both true, and it was after all immaterial whether I chose one form or the other. But the first form was more suitable for experiment and the second form would only be of theoretical value — and so I chose the first form. In order not to get into great difficulties at once, we shall disregard quasi-association for the present, and our result will therefore, at least for the present, be valid only for higher temperatures and not great density.

If we write $p = \pi p_k$, $RT = RT_k m$ and $v = \nu v_k$, and if we put $\frac{RT_k}{p_k v_k} = s$, we derive:

$$\left(\pi + \frac{a}{\nu^2 p_k v_k^2}\right)\left(\nu - \frac{b}{v_k}\right) = ms$$

and as we found $\frac{a}{v_k RT_k} = \frac{f-1}{s}$. or $\frac{a}{p_k v_k^2} = f - 1$, (These Proc. XIII p. 118) we may also write:

$$\left(\pi + \frac{3^{\frac{f-1}{3}}}{\nu^2}\left(\nu - \frac{b}{v_k}\right) = ms\ .$$

In our latest investigations we have shown that

$$s^2 = \frac{64}{27}(f-1)$$

either quite accurately, or with a high degree of approximation. Substituting this, we find:

$$\left(\pi + \frac{3^{\frac{f-1}{3}}}{\nu^2}\right)\left(\nu - \frac{b}{rb_q}\right) = m\frac{8}{3}\sqrt{\frac{f-1}{3}}$$

or

$$\left(\pi + \frac{3^{\frac{f-1}{3}}}{\nu^2}\right)\left(\frac{3\nu}{\sqrt{\frac{f-1}{3}}} - \frac{b}{b_q}\frac{3}{r\sqrt{\frac{f-1}{3}}}\right) = 8m$$

If we put π, ν, $m = 1$, we find:

$$f\left(\frac{3}{\sqrt{\frac{f-1}{3}}}-\frac{b_k}{rb_g}\frac{3}{\sqrt{\frac{f-1}{3}}}\right)=8.$$

With $f=4$ and corresponding $r=3$, we find $\frac{b_k}{b_g}=1$, and with $f=7$ we find:

$$\frac{b_k}{b_g}\frac{3}{r\sqrt{2}}=\frac{3}{\sqrt{2}}-\frac{8}{7}=0{,}978.$$

As $\frac{b_k}{b_g}$ has been found only little smaller than 1, $\frac{3}{r\sqrt{2}}$ will also differ but little from 1; from $rs<8$ follows in the case that $s^2=\frac{64}{27}(f-1)$ is assumed as perfectly accurate, with $rs<8$:

$$r<\frac{8}{s}$$

or

$$r<\frac{8}{\frac{8}{3}\sqrt{\frac{f-1}{3}}}$$

$$r<\frac{3}{\sqrt{\frac{f-1}{3}}}$$

Hence

$$\frac{3}{r\sqrt{\frac{f-1}{3}}}>1$$

But it is to be expected that the value of $\frac{3}{r\sqrt{\frac{f-1}{3}}}$ will be only little greater than 1. For $f=4$ with $r=3$ we find it exactly equal to 1 and with $f=7$ we find a value of r little smaller than would follow from $r\sqrt{2}=3$, namely $r=2{,}1213$. We accordingly determined this value at about 2,09. But then we conclude at the same time that if f should have risen to 10, the value of r would descend to below $\frac{3}{\sqrt{3}}=1{,}73$. At all events in the equation:

$$\left(\pi+3\frac{\frac{f-1}{3}}{v^2}\right)\left(3\frac{v}{\sqrt{\frac{f-1}{3}}}-\varphi\frac{b}{b_g}\right)=8m$$

the factor φ will indeed be somewhat greater than 1, but differ only little from 1.

If we confine ourselves to that part of the whole region where no quasi-association worth mentioning is to be expected, to which part the critical point also belongs, the last equation will hardly change, if we put unity in it instead of $\varphi\frac{b}{b_k}$. And then a rule follows from this holding for all normal substances, so for not *really* associating substances, viz. for given π and m, $\frac{v}{\sqrt{\frac{f-1}{3}}}$ has the same value. For substances with the same value of f—1, v is therefore also the same and with different value of f—1 we have

$$\frac{v}{\sqrt{\frac{f-1}{3}}}=\frac{v'}{\sqrt{\frac{f'-1}{3}}}$$

or according to results obtained in These Proc. p. 903.

$$\frac{v}{\sqrt{\frac{b_q}{b_{lim}}}}=\frac{v'}{\sqrt{\left(\frac{b_g}{b_{lim}}\right)'}}.$$

Not rigorously valid for the whole region, however. To equal reduced pressure and temperature corresponds a volume which in reduced measure is different for the different substances, when $\frac{b_g}{b_{lim}}$ differs. But if we write the value $\frac{v}{r\frac{b_q}{b_{lim}}}$ for v, and the value $\frac{v'}{r'\left(\frac{b_g}{b_{lim}}\right)'}$ for v', we obtain:

$$\frac{v}{b_g\, r\sqrt{\frac{b_q}{b_{lim}}}}=\frac{v}{b_g\, r'\sqrt{\left(\frac{b_q}{b_{lim}}\right)'}}.$$

And as we have concluded to the approximate equality of 3, $r\frac{b_q}{b_{lim}}$, $r'\left(\frac{b_q}{b_{lim}}\right)'$ etc. we find as approximate rule: At the same reduced temperature and pressure the same volumes are for all substances the same number of times the molecular volume viz. b_q. If, therefore, we had expressed the law of corresponding states in the second way, it might have been maintained unchanged for all normal substances, at least over a large part of the whole region.

The meaning of equation $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}} = \frac{v'}{\sqrt{\left(\frac{b_g}{b_{lim}}\right)'}}$ is of course this that e,g. for the reduced volume, which in the system in which $f = 4$ is put equal to v_1, $v_1 \sqrt{\frac{b_g}{b_{lim}}}$ must be taken in the system, where $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$. Thus the critical volume is equal to $3b_g$, if $f = 4$ and the reduced volume is then equal to 1. But in the system in which $f = 7$ this volume would have the value of $\sqrt{2}$ in critical measure. That the reduced volume is found $\sqrt{2}$ times larger is due to this that we have divided by a $\sqrt{2}$ times smaller factor.

Hence the different π, m, v surfaces for substances, for which $\frac{b_g}{b_{lim}}$ might differ, do not cover each other, but they can be made to overlap for the greater part, almost entirely, if we divide the value of v by $\sqrt{\frac{b_g}{b_{lim}}}$.

Then, however, the border lines, the loci of the coexisting vapour and liquid phases have not been made to cover each other. Not even by approximation, for this locus, which is determined by

$$p\,(v_2 - v_1) = \int_{v_1}^{v_2} p\,dv\;,$$

also requires the knowledge of the properties for smaller volumes, and will, therefore, also demand the knowledge of presence or absence of quasi-association, but especially the knowledge of the course of $\frac{b}{b_g}$. But this will be discussed later.

The cause of the circumstance that the above mentioned properties only hold by approximation is clearly to be seen, if it is borne in mind that the quantity $\frac{b}{b_g}$ in the form found for the equation of state:

$$\left(\pi + 3\,\frac{\frac{b_g}{b_{lim}}}{v^2}\right)\left(\frac{3v}{\sqrt{\frac{b_g}{b_{lim}}}} - \frac{b}{b_g}\,\frac{3}{\sqrt{\frac{b_g}{b_{lim}}}}\right) = 8m$$

is not constant as soon as $\frac{b_q}{b_{lim}} > 1$. If very large volumes are concerned, we may put 1 for it, and even in the critical volume, viz. $r\,b_q$, the difference with 1 is still slight, and we find from:

$$\frac{b_k}{b_q} = r_{kr}\left(1 - \frac{\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}}{1+3\frac{b_q}{b_{lim}}}\right)$$

for $\frac{b_q}{b_{lim}} = 2$ the value of $\frac{b_k}{b_q}$ to be equal to 0,97 or 0,96.

We conclude from this that for the vapour volumes of the border line the rules given above hold with a high degree of approximation. But for the liquid volumes $\frac{v}{\sqrt{\frac{b_q}{b_{lim}}}}$ is smaller than would be calculated if we had retained $\frac{b}{b_q} = 1$, and the density of the liquid greater. The limiting liquid volume is even not b_g, but b_{lim}, and so $\frac{b_g}{b_{lim}}$ times smaller, and the limiting liquid density $\frac{b_q}{b_{lim}}$ times greater.

This must bring about a change in the value of the factor γ. And we can calculate the value of this change.

Let us put

$$\frac{\varrho_{gas} + \varrho_{vl}}{2\varrho_{kr}} = 1 + \gamma\,(1-m)$$

and for b constant

$$\frac{\varrho'_{gas} + \varrho'_{vl}}{2\varrho'_{kr}} = 1 + \tfrac{1}{2}\,(1-m).$$

At very low temperatures the gas densities disappear. With subtraction of the two equations we find:

$$\frac{\varrho_{vl}}{2\varrho_{kr}} - \frac{\varrho'_{vl}}{2\varrho_{kr}} = (\gamma-\tfrac{1}{2})\,(1-m).$$

For $m = 0$ we must introduce the limiting liquid density, and we get:

$$r\frac{b_g}{b_{lim}} - 3 = (2\gamma-1)$$

or

$$r\frac{b_q}{b_{lim}} = 2(\gamma+1)$$ [1]

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[1] These Proc. p. 903.

As $r\sqrt{\frac{b_q}{b_{lim}}}$ is somewhat smaller than 3, we get:

$$\frac{3}{2}\sqrt{\frac{b_q}{b_{lim}}} \geqq (\gamma+1)\,.$$

Hence the variability of b is the cause that the law of corresponding states does not hold perfectly for all volumes. If this variability was governed by one law, and if accordingly $\frac{b_q}{b_{lim}}$ was the same for all substances, it would hold perfectly. For then the value of $\frac{v}{\sqrt{\frac{b_q}{b_{lim}}}}$ and so also of v would be the same for given π and m. If the law of the variability of b, hence $\sqrt{\frac{b_q}{b_{lim}}}$, is different, then v is indeed not equal for given π and m, but the law of correspondence, as we have stated it here, holds with a high degree of approximation, at least for volumes $> v_k$. Then for given π and m the value of $\frac{v}{\sqrt{\frac{b_q}{b_{lim}}}}$ is almost the same or $\frac{v}{v_k\sqrt{\frac{b_q}{b_{lim}}}} = \frac{v}{r\,b_g\sqrt{\frac{b_g}{b_{lim}}}} = \frac{v}{3b_q}$.

As the volume decreases, the law begins to fail. For $v > v_k$ it holds almost good, below this the deviation becomes greater and greater. The value of b/b_{lim}, however, does not seem to differ much for the different substances. It is not equal to 1 for any substance, not even for monatomic ones. So substances for which b is constant, are only fictions. When, therefore, in my continuity I calculated the critical circumstances keeping b constant, this did not take place because I thought that b would be invariable, but in the expectation that in the critical volume the quantity b would have changed so little that the influence of the change would be inappreciable. And as we have found now, the quantity

$$\frac{b_k}{b_q} = \frac{3}{\sqrt{\frac{b_q}{b_{lim}}}} = \frac{8}{1+3\frac{b_q}{b_{lim}}}$$

is, indeed, not much smaller than 1 for π and $m = 1$. And even if we should assign to $\frac{b_q}{b_{lim}}$ a value so excessively high as would be the case if we put it at 3 — and substances for which this value would occur will, no doubt, have to be looked upon as fictions —

we should still find $\frac{b_k}{b_g} > 0.93$. The reason, therefore, that even for great densities the law of correspondence is fulfilled by approximation will be owing to this that $\frac{b_g}{b_{lim}}$ does not differ much for the different substances. Moreover the region in which the deviations would become of importance, is inaccessible to experiment; e. g. for the liquid volumes which could coexist with vapour volumes at values of $m < \frac{1}{2}$, or for volumes under an excessively high pressure.

We shall add a few more remarks.

That the coincidence of the surfaces $\frac{v}{\sqrt{\frac{b_q}{b_{lim}}}} = f(\pi, m)$ for great values of v entirely disappears for v very small and near v_{lim}, will be clear if we pay attention to the fact that for $\sqrt{\frac{b_q}{b_{lim}}} = 1$ the surface has no points below $v = \frac{1}{3}$; for then $v^{lim} = b_g$ and $v_k = 3b_q$. For $\sqrt{\frac{b_a}{b_{lim}}}$ equal to a value greater than 1, $v_{lim} = b_{lim}$ and $v_k = rb_g$, or

$$v_{lim} = \frac{1}{r}\frac{b_{lim}}{b_g} \text{ and } \frac{v_{lim}}{\sqrt{\frac{b_g}{b_{im}}}} = \frac{\frac{b_{lim}}{b_g}}{r\sqrt{\frac{b_g}{b_{lim}}}} = \frac{1}{3}\frac{b_{lm}}{b_g}.$$

If e.g. $\frac{b_g}{b_{lim}} = 2$, we have obtained new points for the v surface, and the surface begins at $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}} = \frac{1}{6}$. It will be obvious that in such circumstances with difference of the value of $\frac{b_g}{b_{lim}}$ there can be no question of coincidence. There is only perfect coincidence with equality of $\frac{b_g}{b_{lim}}$. If this value differs, the surfaces almost coincide, indeed, for large value of v, but for very small value of v the $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$

ordinates will contract and approach to zero as $\frac{b_g}{b_{lim}}$ becomes larger in a region, however, which is hardly accessible to experiment.

Another remark.

From the circumstance that the $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ surfaces may be considered to coincide, especially for large value of v, it should, however, not be concluded that the border lines coincide. The top differs already. The top lies at π, m, and v equal to 1, and so $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ differs; and great differences are even derived for the gas-branch at low temperatures from the relation which holds approximatively, $-l\frac{p}{p_k}=f\frac{1-m}{m}$. Thus we find in the region where the law of the rarefied gases would hold:

$$-l\frac{8}{3}m\frac{\sqrt{\frac{b_g}{b_{lim}}}}{v}=\left(1+3\frac{b_g}{b_{lim}}\right)\frac{1-m}{m}.$$

Hence in a region where correspondence would perfectly prevail the border lines differ exceedingly much. This is of course the consequence of the liquid volumes no longer corresponding when $\frac{b_g}{b_{lim}}$ differs, and the construction of the border line also requires the knowledge of these volumes. Where the gas-laws hold, $\frac{pv}{RT}=1$, or $\frac{\pi v}{m}\frac{p_k v_k}{RT_k}=1$, and now we have come to the conclusion that $\frac{RT_k}{p_k v_k}$ for the different substances is equal to $\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$. Then

$$\frac{\pi v}{m}=\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$$

or

$$\frac{\pi}{m}\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}=\frac{8}{3}$$

A confirmation of the thesis, that the π, m, $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ surfaces coincide for great value of v.

Now the important question is still left undecided, in how far does the value of $\frac{b_q}{b_{lim}}$ differ for the different substances. We have already stated that it is not probable that there are substances for which this quantity $=1$. These substances have sometimes been called *perfectly hard* substances, but then it should be borne in mind that since it has appeared that $f > 4$ and $s > \frac{8}{3}$ for monatomic substances, even monatomic substances would not be perfectly hard. For all substances, with our present knowledge we may say without exception, $\frac{b_q}{b_{lim}} > 1$, and probably not very different from 2. Now we might account for about 2 by assuming *quasi-association*. In large volume b_q is the fourfold of the volume of the molecules; hence if the spherical shape is assumed and the diameter is put $= \sigma$, $b_q = 4\frac{\pi}{6}\sigma^3$. The limiting volume of the substance is present when the pressure is infinite at temperatures $T > 0$. Then the molecules must touch, and the volume is only little smaller than σ^3 or $b_{lim} \leqq \sigma^3$. Hence:

$$b_q \geqq \frac{2\pi}{3} b_{lim}$$

or $b_q \geqq 2{,}09\, b_{lim}$.

But on the other hand we should consider that often

$$\frac{b_q}{b_{lim}} < 2.$$

If not the spherical shape was assumed, but as extreme case, a rectangular shape, b_q would be $= 4\sigma^3$, and $b_{lim} = \sigma^3$, and $\frac{b_q}{b_{lim}} = 4$. This will, probably, not be expected by anybody. For ellipsoidal shape we should again find a little more than 2. In this way it seems impossible to me to explain the value of $\frac{b_q}{b_{lim}} < 2$. But we shall possibly discuss this later.

The original theorem of the corresponding states pronounced the equality of the π, μ, ν surface. In the form given here it states the superposition of the $\pi, m \dfrac{\nu}{\sqrt{\dfrac{b_q}{b_{lim}}}}$ surfaces. These two forms would coincide, if there was only one single law for the course of b. In the form given here the ν ordinates are only $\frac{b_g}{b_{lim}}$ times smaller. But the advantage of the form given here is obvious, when there are different kinds of substances from the point of view of the law of correspondence. First of all it points out the cause for the existence of these different kinds, about which cause the form given originally does not reveal anything. Secondly it appears that attempts to find perfect correspondence between these different kinds must fail, and have certainly no chance of success by variations in the π and m ordinates. And thirdly it shows that the deviation between the different kinds of substances is a gradual one, and the coincidence in the rarefed gas-state is restored.

Physics. — *"On the* HALL-*effect, and on the change in resistance in a magnetic field at low temperatures.* VI. *The* HALL*effect for nickel, and the magnetic change in the resistance of nickel, mercury and iron at low temperatures down to the melting point of hydrogen".* By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N°. 132*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of November 30, 1912).

§ 17.[1] *Magnetic change in the resistance of solid mercury.* The resistance was measured of mercury contained in a glass capillary 9 cms. long, and of 0.12 mm. diameter. The capillary was U-shaped, and to either end were fused two glass leading tubes which were filled with mercury. The resistances were measured by the KOHLRAUSCH method of overlapping shunts, in which the main current was $I = 0.006$ amp. The mercury was frozen by blowing cooled hydrogen vapour into the cryostat through a glass tube whose lower extremity reached below the resistance. The resistance was found to be

7,97 Ω at $T = 287°,3$ K.
0,1014 $T = 20°,3$
0,0618 $T = 14°,5$

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[1] The sections of this paper are numbered in continuation of those of Comm. N°. 130*c* (Oct. 26, 1912).

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