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temperature one has to take the (practically) constant velocity, when the experiment is rightly performed, sets in after a short period.

5. The thus studied velocity shows also in absence of (last) noxious influences, an optimum for a certain temperature, which is contrary to the theory of DUCLAUX-BLACKMAN for the explanation of the occurrence of a temperature optimum at physiological elements, this theory should hence be rejected.

6. The diffusion through the wall of the yeast cells is not a limiting factor in the processes studied by us.

7. The fact that also physico-chemical reactions deviate from the rule of VAN 'T HOFF cannot be opposed to our conclusion that in the case of the alcohol fermentation, the considerable deviation from that rule beneath noxious temperatures is in contradiction with the theory of DUCLAUX-BLACKMAN.

8. On the contrary, it speaks greatly in favour of our observations and conclusions that the catalysis of hydro-oxygen-mixtures by colloidal platinum (which process presents also in other respects much analogy to physiological katabolisms) shows a temperature optimum in the absence of (lasting) noxious action, so on exclusion of the time factor behaves with respect to the temperature perfectly in the same manner as was found by us for the alcohol fermentation and the inversion of cane sugar by yeast invertase.

Delft, October 1910.

**Physics.** — "*Isotherms of monatomic gases and of their mixtures. VI. Coexisting liquid and vapour densities of argon. Calculation of the critical density of argon.*" By C. A. CROMMELIN. Comm. N<sup>o</sup>. 118<sup>r</sup> from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of September 24, 1910).

§ 1. The experiments published a short time ago<sup>1)</sup> by which the vapour pressures of argon above —140° C. were determined by a means of deriving the difference between the coexisting liquid and vapour densities at the same temperatures as those at which the vapour pressures were measured. As was mentioned in § 2 of the paper just referred to, both the position of the argon meniscus in the low temperature reservoir and that of the mercury meniscus

<sup>1)</sup> These Proceedings May 1910. Comm. Phys. Lab. Leiden, N<sup>o</sup>. 115. For this paper which is frequently quoted in the text will be called Comm. 115.

in the stem of the piezometer (immersed in a water bath at about 20° C.) were read off in the two measurements that formed each vapour pressure determination. As the cross-sections of the reservoir and of the piezometer stem were known and the temperature of the waterbath was noted, and as, moreover, the density of the gaseous argon in the stem could be calculated from argon isotherms which will soon be published by Prof. KAMERLINGH ONNES and myself<sup>1)</sup>, all the data necessary for the calculation of the difference between the liquid and vapour densities were known. For the mass of the gas by which the quantity in the stem has been lessened during condensation is equal to the mass of liquid formed *minus* the mass of saturated vapour that at the beginning of condensation occupied the space taken up at the end of condensation by the liquid that has been formed. In the calculation a correction has been made for the volume of the glass stirrer in the low temperature reservoir

§ 2. The *results* lay no claim to an accuracy equal to that of the vapour pressure determinations in the paper referred to. The accuracy can be estimated at from 1 to 1½ %, but the fact that nothing is known concerning the liquid and vapour densities of argon in the region covered by my experiments seemed to me to justify the publication of these results. The calculations (in which, of course, allowance was made for the small impurity in the argon) could be made only for series VI, V, III, and IV, and II of Comm. 115, since the temperature in the two series VIII and IX was in the immediate neighbourhood of the critical temperature, and the meniscus was too unsteady to allow of fairly sharp readings.

The results obtained are collected in the following table. As usual the subscripts 1 and 2 refer to the liquid and vapour states respectively; the densities are given with respect to water at 4° C.

Date	Series	$t$	$p^2)$	$d_1-d_2$
1910. 10 Febr.	VI	-140.80	22.185	0.9195
10 »	V	-134.72	29.264	7718
9 »	III and IV	-129.83	35.846	6502
9 »	II	-125.49	42.457	4714

<sup>1)</sup> In the present paper frequent use is made of these isotherms.

<sup>2)</sup> For the sake of completeness vapour pressures (already published in Comm. 115) are here inserted in the table.

§ 3. *Deduction of the values of  $d_1$  and  $d_2$ .* Now that  $d_1 - d_2$  is known, the values of  $d_1$  and  $d_2$  may be reached by assuming that the CAILLETET and MATHIAS<sup>1)</sup> law of the rectilinear diameter holds for argon. Considering that the accuracy of the experiments with which we are at present concerned is not very great we may quite well base our calculations on this assumption, the more so as MATHIAS and KAMERLINGH ONNES<sup>2)</sup> have just shewn from very accurate measurements that oxygen obeys this law. The applicability of this law to argon, therefore, is not necessarily called into question by the fact that the critical temperature of argon is much lower than is the case with substances for which the validity of the law of the rectilinear diameter has been experimentally established.

To be able to apply this law, however, to our present purpose, we must know the data for the diameter with considerable accuracy. They can be deduced only very inaccurately from the liquid densities given by BALY and DONNAN<sup>3)</sup> which were used along with the diameter in Comm. 115 for determining the critical density. Their measurements, moreover, cover a range of only 6°, viz. from -189° C. to -183° C. far removed from the critical temperature, and a difference of 0.2% between the errors in their extreme observations causes an error of about 3% in the critical density. And further, a small percentage error in the critical density is greatly magnified in the vapour volumes e. g. at -130° C. about 4 times, at -134° C. about 7 times and at -140° C. about 13.5 times. When the values of  $d_1$  and  $d_2$  calculated from the estimate of  $d_k$  (0.496) based on BALY and DONNAN'S results, which was used in Comm. 115, and the points on the boundary curve deduced from them were accordingly plotted in the  $pv$ -diagram of the argon isotherms and along with them experimental values of the vapour volumes obtained by slight extrapolation of accurate isotherms, it was seen that they deviated considerably from each other.

I tried therefore to obtain  $d_k$  independent of BALY and DONNAN with a view to finding the constants of the diameter from their liquid densities regarded as a determination of  $d_1 + d_2$  for a single temperature far from the critical. This can be done with the help of the vapour pressures published in Comm. 115 and of the argon isotherms that are still to be published mentioned in § 1 of the present paper.

At the critical point the equation :

<sup>1)</sup> L. CAILLETET and E. MATHIAS Journ. d. Phys. (2) 5, 549, 1886.

<sup>2)</sup> Zitt.versl. Juni 1910. C. R. Ac. d. Sc. Paris 151, 213 and 474, 1910.

<sup>3)</sup> E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. 81, 911. 1902.

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{\text{coex}} \quad \dots \quad (A)$$

holds.

$\left(\frac{\partial p}{\partial T}\right)_v$  is with great approximation independent of temperature<sup>2)</sup>; its values for successive densities in the neighbourhood of the critical density were read from a  $pv$ -graph of accurate isotherms just above the critical point. Hence these values hold, too, for the critical temperature itself. The value of  $\left(\frac{dp}{dT}\right)_{\text{coex},k}$  can be deduced from data published a short time ago<sup>3)</sup> viz:  $\left(\frac{dp}{dT}\right)_{\text{coex},k} = 1.820$ . Interpolation between the values of  $\left(\frac{\partial p}{\partial T}\right)_v$  obtained from the isotherms gave in this way 0.509 as the density for which equation (A) holds.

In connection with the deduction of this value, however, it must be remembered that this method has already led repeatedly to a result for  $d_k$  differing from that found from the diameter, and that the results obtained by the two methods deviate so far from each other that the difference cannot be attributed to errors of observation or calculation. The values obtained according to these two methods must therefore be regarded as experimental data differing in general from each other and each of them deduced in a certain way. For instance, KEESOM<sup>4)</sup> found 0.00418 for the experimental critical volume of carbon dioxide (expressed in the theoretical normal volume as unit) using the law of the diameter, and 0.00443 for the volume for which equation (A) holds. And KAMERLINGH ONNES and KEESOM<sup>5)</sup> mention that BRINKMAN<sup>6)</sup> found a similar difference in the case of carbon dioxide and of methyl chloride, as MILLS<sup>7)</sup> did for ethyl aether, isopentane and normal pentane. These deviations are such

<sup>1)</sup> M. PLANCK, Ann. d. Phys. (4). 15. 457. 1882. KEESOM (Proc. Dec. 1901 Comm. 75) mentions three proofs communicated to him by Prof. VAN DER WAAALS. One of them can be found in VAN DER WAAALS—KOHNSTAMM, Lehrbuch der Thermodynamik. I, p. 35 and 36.

<sup>2)</sup> cf. W. H. KEESOM, Proc. Jan. 1904. Comm. N<sup>o</sup>. 88, (pg. 54). Thesis for the doctorate, Amsterdam 1904. p. 86.

<sup>3)</sup> Comm. 115, last page.

<sup>4)</sup> l. c.

<sup>5)</sup> Proc. Febr. 1908. Comm. N<sup>o</sup>. 104a, see also H. KAMERLINGH ONNES and Miss T. C. JOLLES. Proc. Febr. 1907, Suppl. 14.

<sup>6)</sup> C. H. BRINKMAN, Thesis for the doctorate, Amsterdam. 1904, p. 43.

<sup>7)</sup> MILLS, Journ of phys. chem. 8. 594 and 685. 1904.

that the method of the diameter gives the smaller value for the critical volume. It was the deviation between the results obtained by these two methods that led KAMERLINGH ONNES and KEESOM to undertake the study of the disturbance function which must ascribe a mutual relationship to these and similar deviations. Until it shall appear that this is not the case with argon and it shall be found that the two values agree, as is not impossible for this substance, we must assume that the above value ( $d_k = 0.509$ ) is smaller than that which would be given by an application of the diameter law to observations in the neighbourhood of the critical temperature, and this latter value is just the one that we require for our present calculations. In the meantime, however, there is no other course open to us than to base our calculations upon the value just given,

$$d_k = 0.509.$$

In this treatment of the question we neglect a difference which, if it could be considered equal to the differences usually existing between values of critical density as determined by these two methods would be much greater than that between the newly derived value and that used in Comm. 115 ( $d_k = 0.496$ ).

As was mentioned in the beginning of this section a small change in the value of  $d_k$  is sufficient to cause a large alteration of vapour volume, and it is accordingly remarkable that a good agreement is obtained between the observed values and those calculated with the value of  $d_k$  now deduced. We must ascribe this to the fact that a value of  $d_k$  happens to have been found which is very suitable for the representation of coexisting liquid and vapour densities by the diameter, and this further leads us to suspect that the two methods of determining the critical density of argon will give results that differ but slightly from each other.

The calculations were made as follows: the diameter was drawn from the observations of BAILY and DONNAN in the neighbourhood of the boiling point of argon using the above value of  $d_k$ , and the critical temperature lately published, — 122°.44 C. From the graph were read values of  $\frac{1}{2}(d_1 + d_2)$  and from these and the observed values of  $d_1 - d_2$ ,  $d_1$  and  $d_2$  were calculated. The results are given in the following table. For the sake of completeness there are also inserted in the table densities  $d_{A_1}$  and  $d_{A_2}$  in terms of the normal density (the wt. of 1 l. of argon = 1.782 g. under normal conditions according to RAMSAY and TRAVERS<sup>1</sup>) and volumes  $v_{A_1}$  and  $v_{A_2}$ , in

<sup>1</sup>) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329, 1900, . . . . .

terms of the normal volume; these volumes served along with vapour pressures known from Comm. 115 for the construction of the boundary curve in the  $pv$ -diagram.

Series	$d_1$	$d_2$	$d_{A_1}$	$d_{A_2}$	$v_{A_1}$	$v_{A_2}$
VI	1.0268	0.1073	576.2	60 21	0 001735	0 01661
V	0.9339	1621	524.1	90 97	1908	1099
III en IV	8581	2079	481 6	116 67	2076	08571
II	7557	2843	424.1	159 54	2358	06268

In the accompanying figure are given curves for the liquid and vapour densities and for the diameter constructed from the above values of  $d_k$ ,  $d_1$  and  $d_2$ , the liquid densities given by BALY and DONNAN and the critical temperature — 122°.44 C. of Comm. 115.

The unconstrained manner in which the curves could be drawn through the points shewed that in the case of argon there was no necessity to expect any great deviation from the diameter law upon which the calculations were based.

Only the points of Series V (— 134°.72) do not appear to fit the curve so well, which is no doubt explained by an error of observation.

#### § 4. Representation of the observations by formulae.

a. The purely empirical formula given by KEESOM<sup>1)</sup> is the most suitable one for this purpose; it may be written in the form

$$\left. \begin{aligned} \frac{d_1}{d_k} &= 1 + A(1-t) + B(1-t)^\lambda \\ \frac{d_2}{d_k} &= 1 + A(1-t) - B(1-t)^\lambda \end{aligned} \right\} \dots \dots \dots (1)$$

in which  $A$ ,  $B$ , and  $\lambda$  are constants, and  $t$  represents reduced temperature.

By subtracting these equations the following simple relation is found for the observed magnitude  $d_1 - d_2$ :

$$d_1 - d_2 = 2d_k B(1-t)^\lambda.$$

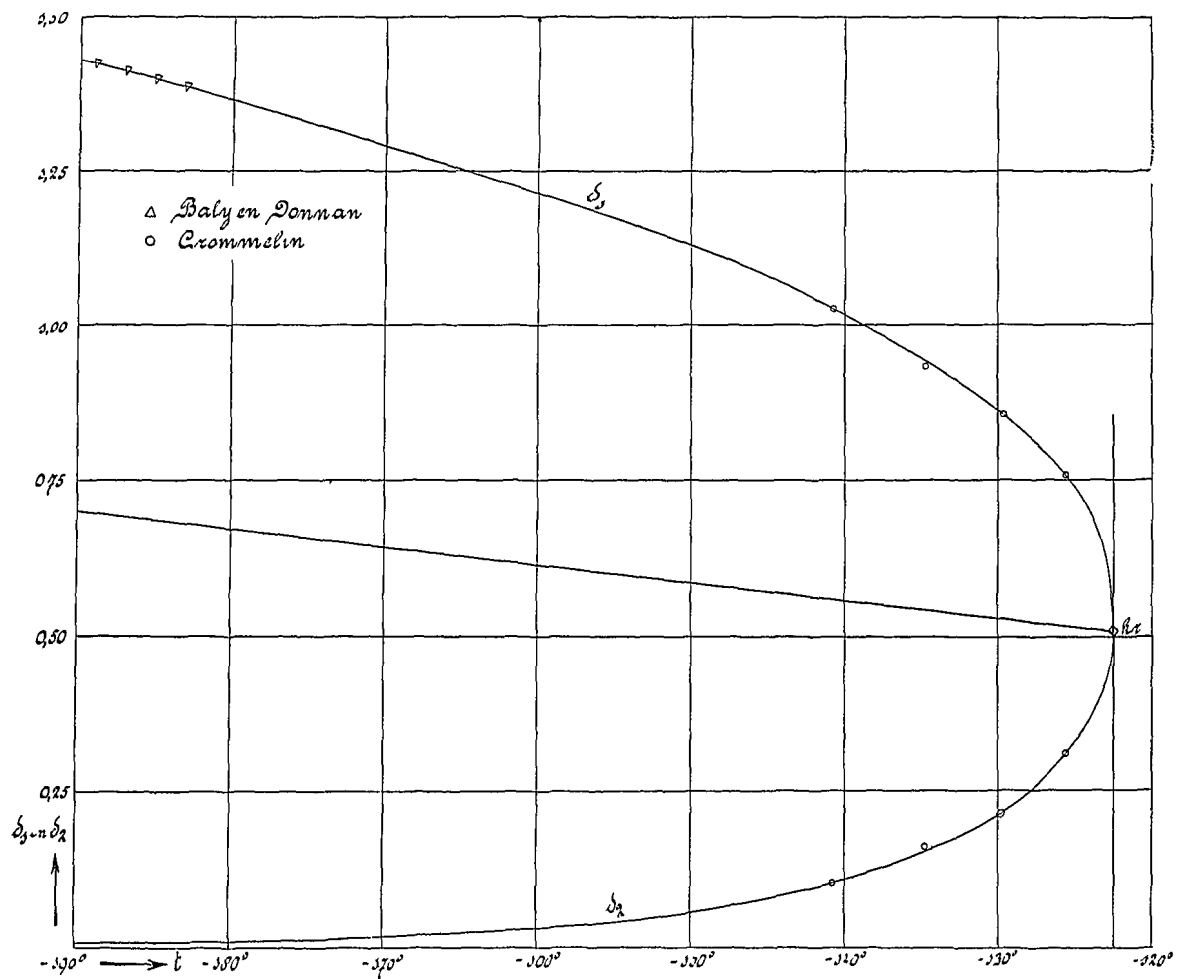
With constants

$$\lambda = 0.3795 \text{ and } B = 1.999$$

determined by the observed values the following correspondence is obtained:

<sup>1)</sup> W. H. KEESOM, Proc. April 1902, Comm. No. 79.

C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures.  
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Proceedings Royal Acad. Amsterdam. Vol. XIII.



Series	$d_1-d_2$ (O)	$d_1-d_2$ (C)	O-C abs.	O-C in %
VI	0.9195	0.9172	+ 0.0023	+ 0.2
V	7718	7874	- 0.0156	- 2.0
III and IV	6502	6493	+ 0.0019	+ 0.3
II	4714	4641	+ 0.0073	+ 1.5

we calculate the constant  $A$  of (1) from the values of  $d_1$  and  $d_2$  deduced in § 3, the following correspondence is found for  $d_1$  and  $d_2$  expressed by equation (1) with the value  $A = 0.9758$ .

Series	$d_1$ (O)	$d_1$ (C)	O-C abs.	O-C in %	$d_2$ (O)	$d_2$ (C)	O-C abs.	O-C in %
I	1.0268	1.0272	-0.0004	0.0	0.1073	0.1119	-0.0046	- 4.2
	0.9339	0.9424	-0.0085	- 0.9	1621	1566	+0.0055	+ 3.4
dIV	8581	8574	+0.0007	+ 0.1	2079	2094	-0.0015	- 0.7
	7557	7506	+0.0051	+ 0.7	2843	2875	-0.0032	- 1.1

These equations therefore give such results as might reasonably be expected from the accuracy of the observations. Slightly better results could of course be obtained by using least squares. The fact that the deviations of series V are on the whole greater than those of the other series may be explained by the suspicion already expressed that an error of observation has been made in that series.

GOLDHAMMER's <sup>1)</sup> formula, for  $d_1-d_2$ , is

$$d_1 - d_2 = m d_k (1 - t)^{3/2}$$

with  $m = 3.496$  the following correspondence is obtained:

Series	$d_1-d_2$ (O)	$d_1-d_2$ (C)	O-C abs.	O-C in %
VI	0.9195	0.8840	+ 0.0355	+ 3.8
V	7718	7731	- 0.0013	- 0.2
III and IV	6502	6526	- 0.0024	- 0.4
II	4714	4859	- 0.0145	- 3.1

The correspondence as might be expected is not nearly so good as that with KEESOM's equation.

<sup>1)</sup> D. A. GOLDHAMMER. Zs. f. phys. Chem. 71. 577. 1910.

This formula is almost identical with KEESOM's, for KEESOM gives for pentane 7 as the value of the index which I have called  $\lambda$ . To get as good an agreement as possible, however, I have made an independent calculation of this index.