Dr. J. VERSCHAFFELT. *Measurements concerning the capillary ascension of liquefied gases.*

1. *Method.* The experiments were made with carbonic acid and nitrous oxide. Investigations made by Dr. KUENEN have shown that we may get these two gases quite pure out of the iron cylinders in which they are sold. I therefore purified these gases bij following the method already described by Dr. KUENEN in his paper. [1]) The purification-apparatus is shown by fig. 1. A is the iron cylinder which contains the still impure, liquid gas, B a thick iron tube filled with pentoxide of phosphorus, and C a thick copper-walled cylinder, into which the pure liquid gas is to be collected. The whole apparatus can be emptied of air by means of the mercury air-pump L; the brass cock 6 separates the purifying apparatus from that used for observation.

The arrangement for measuring the capillary ascension is chiefly the same as used by DE VRIES. [2]) The thick glass tube *b* (fig. 2) in which the capillary tube is shut up, supports at its upper end a piece of narrow manometer tube, which itself bears a wider reservoir *g* filled with glasswool; this glasswool is useful for stopping the dust carried away, by the streaming gas, from the junction tubes and cocks Two cork-pieces *k* keep the observation tube well centered in the liquid bath, and support a thermometer *t*.

The upper end of the observation-tube is cemented by means of sulphur in a brasspiece *d*, which is connected through a long steel capillary tube and a cock *m* to a long copper capillary tube *x*, and communicates through the cocks 4 and 5 (fig. 1) with the cylinder C and the air-pump L.

The filling of the observation tube takes place in the following way; cocks 5 and 6 are opened and the tube emptied of air; 5 is afterwards shut and 4 opened. If the temperature in the tube *b* be lower than in the cylinder C, distillation of the liquid takes place from C into *b*; as soon as a sufficient quantity of liquid has been collected in the observation tube, the cocks 4 and 6 are shut again. After this operation the liquid thread in the capillary tube is generally broken, either by residues of air, or by vapour bubbles. The continuity of the thread of liquid could always be obtained by causing the liquid to boil slowly; for this purpose the cocks 5 and 6 were opened a little way; the gas escaped through the safety-manometer *v*.

For observations made at about the temperature of the room, the observation tube was placed in a glass-cylinder having nearly the same length (nearly 1 M.) and a diameter of about 5 cM.; through this cylinder

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[1]) Arch. Néerl., 26, 35; 1893.

[2]) Measurements on the influence of temperature on the capillary elevation of ether between the critical state and the boiling point of ethylene. Dissertation, Leiden 23 Jan. 1893. Arch. Néerl., 28, 212; 1894. Short abstract in Communic. n⁰. 6.

water from the main was conducted, so that it entered at the inferior part, and streamed out at the upper end through a lateral tube. In order to avoid a deposit of moisture on the bath, this was enclosed in a second glasscylinder, and the space left between the two dried by means of pentoxide of phosphorus.

Fig. 2 shows the arrangement when experiments were taken in boiling methylchloride. The glass apparatus is the same as the one used by DE VRIES during his observations made in boiling ethylene; the temperature however being not so low allowed me to leave out some complications.

The observation tube was put in another tube which had nearly the same length, about 1 M., and a diameter of nearly 3 cM.; and which was in connection with a lateral tube down through which the liquid methylchloride was to be poured; both tubes were shut by stopples and rendered quite air-tight by means of collodium elasticum. The main tube *h* has a brass **T**-piece T of nearly the same width, that communicates, through a wide and stiff caoutchouc tube *u*, with bags for keeping the gaseous methylchloride. Through the stopple which shuts the lateral tube *z*, comes a copper capillary tube *r* through which the liquid flows, and a small glass tube that communicates with an air-pump through a thick caoutchouc tube *w*; *f* is a small glasswool filter for purifying the methylchloride. Before any methylchloride is introduced, the apparatus and bags are emptied. Because the space in which the liquid boils communicates with the bags, which support the atmospheric pressure, the methylchloride itself boils under the same pressure; the

small difference however which might arise from the stiffnes of the bags may be read on a differential-manometer; a notable difference I never observed.

All around the inferior part of the main tube are placed several glass cylinders as in the experiments of WROBLEWSKI and OLSZEWSKI. By these glass cylinders the observations are also rendered more safe; after the following experiments were finished, the observation tube burst; the effect was that in the immediate neighbourhood all was broken, the outermost cylinder however remained intact.

2. *Experiments.* The liquid gas being introduced into the observation tube, and after it had boiled for the purpose of eliminating the last bubbles from the capillary tube, its temperature differed always a little from that of the surrounding bath. The thick walls of the observation tube, caused the equilibrium to be reached but very slowly, so that the capillary ascension became constant only after half an hour.

In order that we might be sure that the carefully chosen capillary tube had everywhere the same diameter, capillary ascension was observed at several spots; the diameter had really everywhere the same value. This trial being made once, capillary ascension might in the following experiments be measured at every part of the capillary tube. The following ascensions *h* were observed: the observed ascension is the vertical distance between the lower point of the meniscus in the capillary tube, and the lower point of the meniscus in the annular space, left between the capillary and the observation tube. To estimate the correction, which the ascensions must undergo, the height d of the annular meniscus has also been observed.

I. Carbonic acid.

1°. Temperature of the room; the water bath remained at rest during a long time, till its temperature had become constant:

$t = 20°,9 \qquad h = 4,20$ mM. $\qquad d = 0,61$ mM.

2°. Temperature of the water distribution:

$t = 15°,2 \qquad h = 6,55$ mM. $\qquad d = 0,75$ mM.

3°. Cooled water bath; obtained by conducting the water from the distribution through a copper spiral placed in melting ice:

$t = 8°,9 \qquad h = 9,20$ mM. $\qquad d = 0,88$ mM.

4°. Boiling methylchloride:

$t = -24°,3 \qquad h = 21,75$ mM. $\qquad d = 1,18$ mM.

II. Nitrous oxide.

1°. Temperature of the room:

$t = 19°,8 \qquad h = 6,60$ mM. $\qquad d = 0,72$ mM.

2°. Temperature of the water distribution:

$t = 14°,4 \qquad h = 8,71$ mM. $\qquad d = 0,85$ mM.

3°. Boiling methylchloride:

$t = -24°,0 \qquad h = 23,20$ mM. $\qquad d = 1,24$ mM.

If we make a graphical representation of the heights of ascension, we see that the observations made at the highest temperatures lie upon a straight line which cuts the axis of temperatures at the critical point: 31°,1 for carbonic acid, and 36°,1 for nitrous oxide. The observations made in boiling methylchloride give points

that lie a little below these lines; the ascension curve turns its concavity towards the axis of temperatures.

It is remarkable that, when we transfer the two curves so, that their origins begin at the same point, they coincide almost over their whole length; at the same distance of the critical temperature carbonic acid and nitrous oxide have nearly the same capillary ascension.

We usually consider the meridian section of an annular meniscus as circular; if this supposition is right, the height of this meniscus must have the value $\frac{r_3 - r_2}{2}$ r_3 being the inner radius of the observation tube, and r_2 the outer radius of the capillary tube. I observed $r_3 = 3,30$ mM., and $r_2 = 0,52$ mM.; consequently $\frac{r_3 - r_2}{2} = 1,39$ mM. By representing graphically the d-values, we see that points thus obtained are situated upon a curve, which ascends rapidly from the critical point, and approaches slowly to the limit-value 1,39 mM. at lower temperatures.

3. *Corrections.* The surface energy σ, in ergs, is to be calculated by means of the formula

$$\sigma = \tfrac{1}{2}\, g\, H\, (\rho_v - \rho_d)\, r_1$$

in which are

r_1 the inner radius of the capillary tube in cM.

ρ_v and ρ_d the densities of liquid and vapour.

H the real ascension in cM.

$g = 981,1$.

The real ascension may be obtained from the observed one by means of two corrections; the first, due to the meniscus in the capillary tube, has the value $\frac{r_1}{3}$. I observed $r_1 = 0{,}0873$ mM., consequently $\frac{r_1}{3} = 0{,}029$ mM.

As for the second correction, its signification is this: we observed the distance between the lowest points of both menisci, while we must know the height above an infinite horizontal plane. We therefore must try to determine the distance between that plane and the lowest point of the annular meniscus; if h^1 is that distance, we have

$$H = h + h^1 + \overset{\frac{r_1}{r_3}}{\cancel{0.029}}.$$

Assuming as generally admitted the meridian section of the meniscus to be a circular one, we would have $d = 1{,}39$ mM.; observations have shown that this is not correct.

De Vries [1]) did not succeed in finding out a good basis for making this correction; I believe I have found one in the value of d itself; we feel indeed that this correction is intimately connected with this value. For correcting the ascensions in wide circular tubes we sometimes consider the surface of the meniscus as obtained by the revolution of an ellipse. Let us assume the same hypothesis for our annular meniscus; if the meridian section be really an ellipse, half of the greater axis is then $= \frac{r_3 - r_2}{2} = 1{,}39$ mM., while half the smaller axis is $= d$.

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1) Dissertation, p. 40.

18

If our hypothesis be right, the radial radius of curvature must be

$$\frac{\left(\frac{r_3 - r_2}{2}\right)^2}{d}$$

and the other one is infinitely great. Consequently

$$\tfrac{1}{2}\, g\, (\rho_v - \rho_d)\, h^1 = \frac{\sigma}{2}\left[\frac{d}{\left(\frac{r_3-r_2}{2}\right)^2} \pm \frac{1}{\infty}\right] = \sigma \frac{2d}{(r_3-r_2)^2};$$

and since

$$\sigma = \tfrac{1}{2}\, g\, r_1\, (\rho_v - \rho_d)\,(h + h^1 + \overset{\frac{r_1}{3}}{\cancel{0{,}029}})$$

is

$$h^1 = (h + \overset{\frac{r_1}{3}}{\cancel{0{,}029}})\ \frac{\frac{2d}{(r_3-r_2)^2}}{\cancel{\frac{1}{r_1} \quad \frac{2d}{(r_3-r_2)^2}}}.$$

[illegible]

$$(h + 0{,}029)\frac{\frac{2d}{(r_3-r_2)^2}}{\frac{1}{r_1} - \frac{2d}{(r_3-r_2)^2}}$$

$$\frac{1}{r_1} - \frac{2d}{(r_3-r_2)^2}$$

HK.

By means of these formulae the following table has been drawn:

I. Carbonic acid.

t	h^1	H
$t = 20°{,}9$	$h^1 = 0{,}058$ mM.	H $= 4{,}29$ mM.
15°,2	0,112	6,69
8°,9	0,186	9,41
—24°,3	0,594	22,37.

II. Nitrous oxide.

t	h^1	H
$t = 19°{,}8$	$h^1 = 0{,}109$ mM.	H $= 6{,}74$ mM.
14°,4	0,170	8,91
—24°,0	0,668	23,90.

4. *Surface-energy.* The real ascension thus being determined, we can now proceed to calculate the surface-energy σ. The densities of carbonic acid and nitrous oxide have been taken from CAILLETET and MATHIAS [1]) m represents the reduced temperature.

I. Carbonic acid.

m	$\rho_v - \rho_d$	σ	σ (calculated)
0,9665	0,5430	1,00	1,00
0,9477	0,6341	1,82	1,79
0,9270	0,7203	2,90	2,78
0,8178	0,9631	9,21	9,21

II. Nitrous oxide.

m	$\rho_v - \rho_d$	σ	σ (calculated)
0,9473	0,6092	1,74	1,77
0,9298	0,6712	2,50	2,55
0,8056	0,9983	9,92	9,92

These numbers can be represented by means of a formula

$$\sigma = A\,(1 - m)^B,$$

A and B being constants, ⌉ independent of the liquid; [2]) we find

of which B is

CO_2	$log\ A = 1{,}934$	$B = 1{,}311$
N_2O	$log\ A = 1{,}945$	$B = 1{,}333$

by means of these constants, the column σ (calculated) of the last table has been found.

Let us make a comparison of the constants with those found for some other liquids:

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[1]) Journal de Physique, 2e série, t. 5; 1886.

[2]) See v. D. WAALS, Zeitschr. f. physik. Chem., 13, 716, 1894.

Ethyloxide	$log.\ A = 1{,}761$	$B = 1{,}270$
Benzol	1,839	1,230
Ethylacetate	1,810	1,230
Chlorbenzol	1,827	1,214
Carbontetrachloride	1,811	1,228

we see that the agreement is satisfactory. It is remarkable that for carbonic acid and nitrous oxide, the value of B comes nearer to the theorical value $^3/_2$, found by v. D. WAALS, for temperatures very near the critical one.

The molecular surface-energy is

$$\sigma_M = \sigma\,(M\,v)^{2/3} = \sigma\,\frac{M^{2/3}}{(\rho_v\,)^{2/3}}.$$

M being the molecular weight $= 44$ for carbonic acid and nitrous oxide.

Carbonic acid.

t	σ	ρ_v	σ_M
20°,9	1,00	0,7550	15,0
15°,2	1,82	0,8023	26,2
8°,9	2,90	0,8540	40,2
− 24°,3	9,21	1,0097	114,1

Nitrous oxide.

t	σ	ρ_v	σ_M
19°,8	1,74	0,7580	26,1
14°,4	2,50	0,8006	36,1
− 24°,0	9,92	1,0392	120,5

The theory shows [1]) that for all substances $\frac{d\sigma_M}{dt}$ is

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[1]) J. D. v. D. WAALS; Versl. Kon. Akad. 21, 1881.
H. KAMERLINGH ONNES, " " "
R. EÖTVÖS, Wied. Ann. 27, 448; 1886.
v. D. WAALS. Zeitschr. f. physik. Chem., 13, 713; 1894.

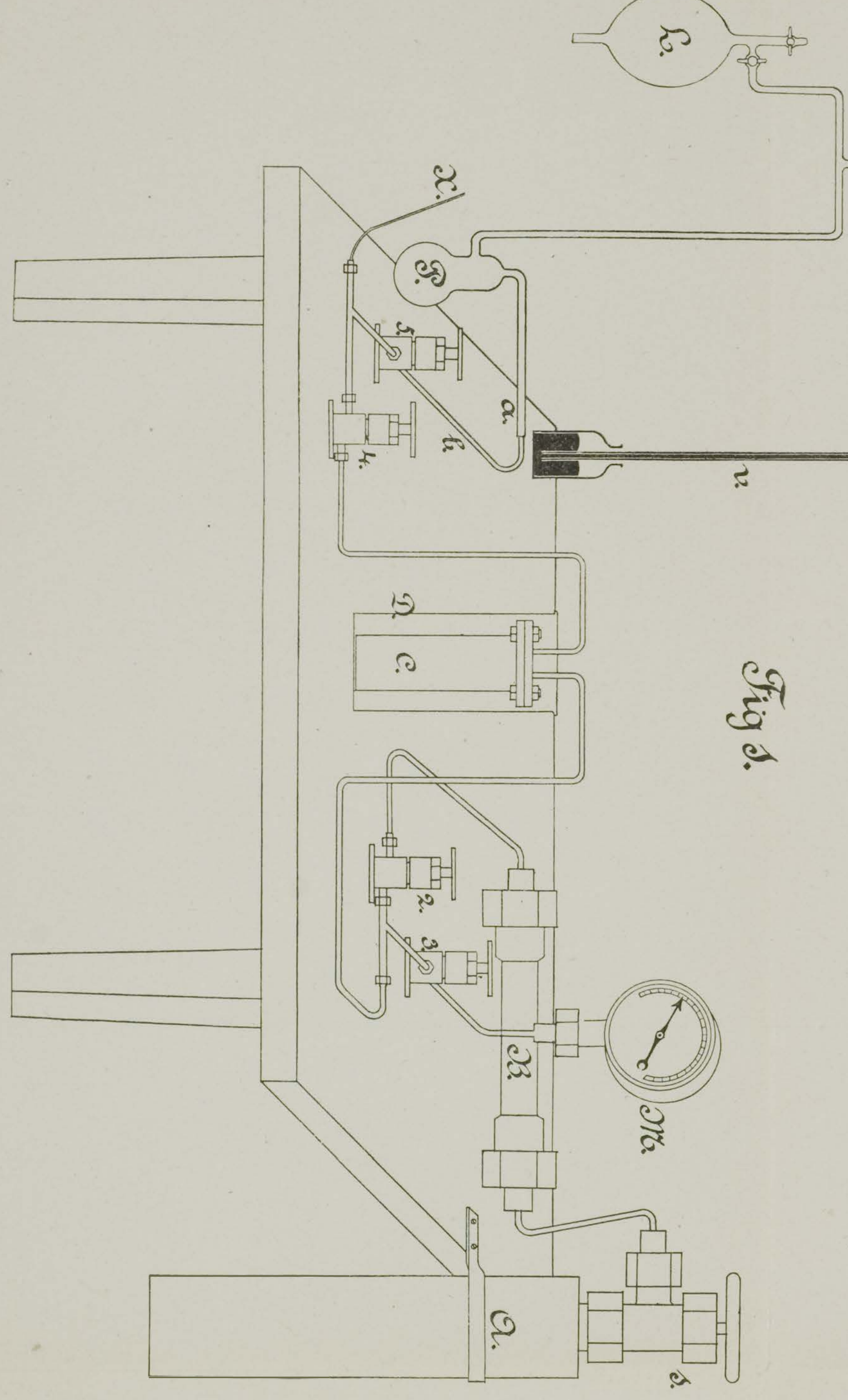

Fig. 1.

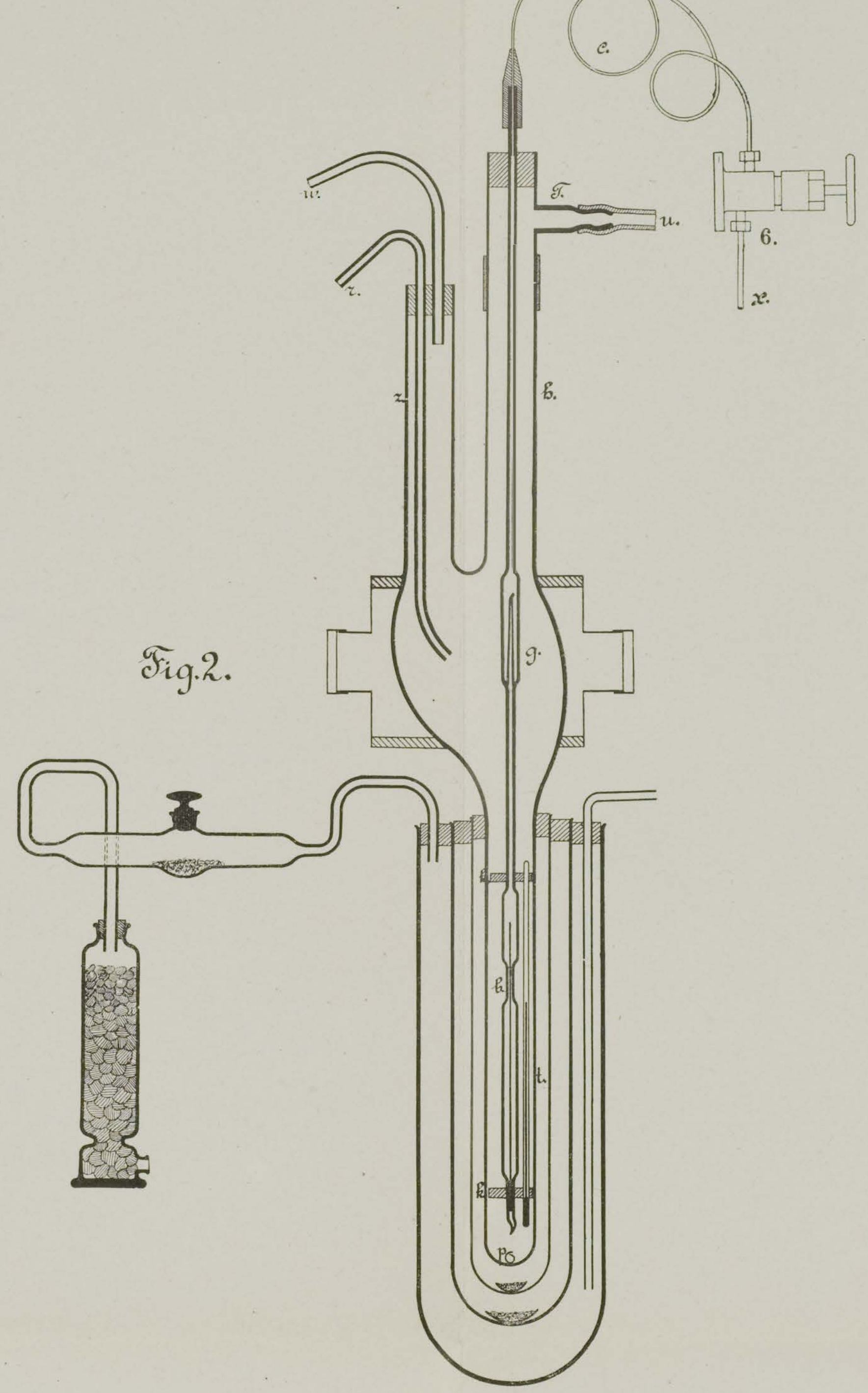

Fig. 2.

Verschaffelt. Capillary Ascension.
Comm. Physical Lab. Leiden. N°. 18.

the same function of the temperature; the experiments have indeed shown that for all substances, at some distance from the critical temperature $\frac{d\sigma_M}{dt}$ is a constant, [1] the value of which is for all liquids nearly the same: mean-value 2,27.

The numbers found above give for carbonic acid

$$\begin{array}{llllll} \frac{d\sigma_M}{dt} = 2{,}222 & \text{between} & 15°{,}2 & \text{and} & 8°{,}9 \\ \phantom{\frac{d\sigma_M}{dt} =} 2.223 & \text{»} & 8°{,}9 & \text{»} & -24°{,}3; \end{array}$$

and for nitrous oxide

$$\frac{d\sigma_M}{dt} = 2{,}198 \qquad \text{between } 14°{,}4 \text{ and } -24°{,}0.$$

Here also the agreement with the law of the corresponding states is very satisfactory.

According to the criterium, given by Ramsay and Shields, for discerning associated from not-associated liquids, carbonic acid and nitrous oxide are to be classed among the not associated ones; that agrees quite with the calculations made by Cailletet and Mathias, [2] concerning the accuracy of the law of the corresponding states for these gases, and the law of the straight diameter.

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[1] R. Eötvös, loc. cit.

[2] W. Ramsay and J. Shields, Zeitschr. f. physik. Chem., 12, 433; 1893.

[3] Loc. cit.

19

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 19.

Dr. A. LEBRET A new method for measuring the Hall-effect, especially the variation of it with temperature.

translated from: "Verslagen en Mededeelingen van de Kon. Akademie van Wetenschappen", van **18 April 1895,** p. 284.)

Dr. A. LEBRET. Dissymmetry of the Hall-effect in Bismuth for the opposite directions of the magnetic field.

(*Translated from the same:* p. 292).

Dr. A. LEBRET. Variation of the Hall-effect in Bismuth with temperature. (*Including an investigation on the variation of the electric Resistance of Bismuth with temperature*).

(*Translated from: "Verslagen en Mededeelingen van de Kon. Akademie van Wetenschappen"* van **28 September 1895,** p. 103, extracted from the inaugural dissertation of **12 July 1895.**)

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