Dr. J. VERSCHAFFELT. *Measurements on capillary ascension of liquefied carbonic acid near the critical temperature.*

In his thermodynamical theory of capillarity [1]), VAN DER WAALS has calculated the value of the surface-energy of a liquid near the critical temperature. He has arrived at the conclusion that, at least at a very short distance from this point, the surface-energy may be represented by a formula

$$\sigma = A\ (1-m)^{3/2}$$

in which A is a constant, and m the reduced temperature.

The values of σ, calculated by means of the experiments of DE VRIES [2]), very well may be represented by a formula $\sigma = A\,(1-m)^B$; B however is not equal to $^3/_2$, but smaller, with a mean value of 1,23, and increases slowly when m comes nearer to 1.

Observations made by RAMSAY and SHIELDS [3]) with a rather great number of liquids, have been used for such calculations [4]). It appeared again that B is never equal

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[1]) Verh. d. Koninkl. Akad. v. Wetensch. te Amsterdam (Eerste Sectie), Deel I, N⁰. 8.

Zeitschr. f. physik. Chem., 13, 1894.

Arch. Néerl., 1894.

[2]) Metingen over den invloed der temperatuur etc., Proefschrift, Leiden, 1893. Communications, n⁰. 6.

[3]) Zeitschr. f. physik. Chem., 13, 1894.

[4]) See v. D. WAALS, loc. cit.

to $^3/_2$, but has a nearly constant value, the same for all liquids.

Many liquids however, investigated till 7° from the critical temperature, give a value of B that increases and even reaches 1,37; this seems to indicate a tendancy to reach the theoretical limit value of 1,5. Others on the contrary, investigated also till a very short distance from the critical point, show no increase of B at all.

In a former communication [1]), in which I have given capillary ascensions of liquid carbonic acid till 10° from the critical temperature, I found $B = 1{,}311$; again a high value. It appeared consequently not uninteresting to pursue these observations nearer to the critical temperature, in order to decide wether the exponent still increases or not.

For such a research carbonic acid seemed to be the most conveniant substance; for its critical temperature may easily be reached, while neighbouring temperatures easily may be kept constant. The desirability of this research has already been pointed out by DE VRIES [2]).

Apparatus. The apparatus used in these researches is substantially the same as used in my preceeding experiments. Some modifications however were rendered necessary by the higher temperature, and the great variability of level of the liquid-surface in the neighbourhood of the critical temperature.

In order to get a suitable temperature a warm waterbath was used. The water of the supply was directed through a copper spiral placed in a waterbath, the temperature of which was kept constant; in this spiral the streaming water reached a temperature that could be raised to the wanted degree, by regulating either the velocity of the circulation or the temperature of the surrounding bath.

The thus heated water entered at the top of a cylindrical space, left between two glass tubes, the inner of which contained the observation tube, and was filled with water in rest. This water became accordingly heated, and when it had reached the state of equilibrium of temperature with the warm water streaming along, it rendered quite insensible the still possible small variations of temperature thereof. It appeared indeed possible to obtain, even above 30°, a temperature varying less than 0°,1. I have moreover observed that the temperature was the same in all sections of the bath.

In order to maintain the surface of the liquid in the middle of the observation tube, this tube was left open at the inferior end, and connected with an hydraulic pump through a pressure-cylinder filled with mercury. The mercury could be driven up through a narrow manometer tube, connected with the narrow manometer tube at the lower end of the observation tube by means of a steel capillary, and two brass pieces in each of which the glass was fastened with sealing wax. The steel capillary was divided in two pieces, joined again by a steel cock, which closed the observation tube when the surface of the liquid had been raised to a convenient niveau; in this way any leakage of pressure-cylinder or pump was rendered harmless. To the inferior part of the observation tube was joined another reservoir the

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[1]) Comm., n⁰. 18.

[2]) Comm., n⁰. 6, p. 7.

volume of which was so chosen, that for a suitable mass of fluid, at all temperatures, the niveau of the mercury could remain in it.

There was still a difficulty to be eliminated, concerning the connection of observation-tube with purifying apparatus. In order to prevent the liquid, distilled over in the apparatus by cooling it beneath the temperature of the room, from distilling over again when raising the temperature, the glass apparatus was shut, immediately above the water-bath, by means of a brass cock, again connected with the glass-apparatus by means of a steel capillary. The connection of this capillary with the glass was not formed as formerly by means of a brass piece fastened with sulphur: for the carbonic acid dissolves the sulphur, as appears from a colouring of the mercury, soon followed by a passing of gasbubbles between glass and metal. The connection was at last made as follows (Fig. 2): at the upper end of the glass-tube a brass piece with screw was fastened with sulphur, glass and metal then rendered quite level, and on the so obtained plane a ring of leather was strongly applied by putting on the screw-nut to which the steel capillary was soldered; this leather ring separated the carbonic acid at the same time from sulphur and free air.

Experiments. — In calculating the surface energy from the capillary ascension, we suppose that in the capillary tube the meniscus is spherical; it is known that this supposition holds only as long as the capillary ascension is at least 20 times as great as the radius. At the critical point the capillary ascension is zero; in order to allow trustworthy values of the surface energy to be obtained as near as possible to this temperature,

among a series of capillary-tubes delivered by GEISSLER, I have chosen the narrowest one, the radius of which was 0,0441 mM.

The pure carbonic acid was obtained in a way already described. A first quantity of this purified gas showed following ascensions:

$t =$ 12°,8	$h =$ 15,36 mM.	$d =$ 0,78 mM.
14°,5	13,92	0,74
16°,5	12,30	0,70
18°,7	10,50	0,64
21°,5	8,24	0,54
25°,3	5,18	0,42
27°,3	3,52	0,34
28°,9	2,20	0,24

d represents the height of the annular meniscus in the wide tube; this height will be taken into account for correcting the ascensions.

In order to ascertain how far these ascensions are to be trusted, I purified a second quantity of gas, and made with it a second series of observations.

$t =$ 15°,9	$h =$ 12,78 mM.	$d =$ 0,74 mM.
20°,3	9,22	0,60
22°,5	7,40	0,52
24°,7	5,68	0,48
26°,6	4,06	0,38
28°,4	2,60	0,28

This second series agrees perfectly with the first. All ascensions lie almost exactly on a straight line, which intersects the axis of temperatures at 31°,6. If therefore the ascensions continued to decrease, with rising temperature, according to a linear law, the critical point, that is the temperature at which $h = 0$, would be about 31°,6. Direct experiments however had shown that the liquid surface vanished at 31°,0. In the immediate neighbourhood of this temperature, this line must therefore be curved towards the axis of temperatures[1]).

In order to determine where the curvature nearly begins, I made a third series of experiments in the

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[1]) The perfect agreement between these two series of observations may not yet be considered as a proof of the purity of the gas. For in both cases the process by which the pure gas has been obtained was quite the same; the two specimens were therefore necessarily of the same degree of purity and should show the same capillary ascension.

That however the gas became more pure by the treatment to which it was subjected, I have proved in making experiments with carbonic acid, directly taken from the box. The capillary ascension was much lower, but different specimens gave also values agreeing with each other:

$t =$ 13°,3	$h =$ 13,40 mM.
15°,9	11,60
17°,4	10,50
20°,3	8,48
22°,4	7,04
23°,2	6,44
26°,1	4,36
27°,5	3,40

Also these ascensions lie upon a straight line, the ordinates of which however are not only smaller than those of the former, but even the point of intersection, 32°,3 is situated further from the true critical one. The purifying of the gas has not only the effect to increase the ascensions, but causes also the straight line upon which they lie to come nearer to the point $h = 0$, $t = 31°,0$. For absolutely pure carbonic acid the line would perhaps meet this point, and the ascensions decrease according to a linear law, till reaching the critical temperature itself.

immediate neighbourhood of the critical point. I succeeded in obtaining a constant temperature at 29°,3, and from that point I made it rise very slowly (nearly 0°,1 in 30 minutes)

$t =$ 29°,3	$h =$ 1,88 mM.	$d =$ 0,20 mM.
29°,7	1,48	0,16
30°,2	1,00	0,12
30°,4	0,74	0,10
30°,5	0,62	0,08
30°,6	0,52	0,06

Though till 30°,9 both menisci could be observed well, yet above 30°,6 observations were rendered impossible by the instability of the meniscus in the capillary; this meniscus was continually in motion, now rising, then falling, even descending beneath the surface of the liquid outside the capillary.

This last series shows clearly a curvature, beginning at ± 29°,5, towards the axis of temperatures.

Applying the correction already used in the former communication:

$$h' = \left(h + \frac{r_1}{3}\right) \frac{\frac{2d}{(r_3 - r_2)^2}}{\frac{1}{r_1} - \frac{2d}{(r_3 - r_2)^2}} = \left(h + \frac{r_1}{3}\right) \frac{2d}{\frac{(r_3 - r_2)^2}{r_1} - 2d}$$

the real ascension is found to be

$$\mathrm{H} = h + h' + \frac{r_1}{3}$$

I found $r_3 = 3{,}25$ mM., and $r_2 = 0{,}280$ mM. Hence

$t =$ 12°,8	$h' =$ 0,120mM.	H = 15,50mM.	H(*calc.*) = 15,48mM.
14°,5	0,104	14,04	14,08
15°,9	0,095	12,89	12,92
16°,5	0,086	12,40	12,43

t = 18°,7	h'=0,067mM.	H =10,58mM.	H (*calc.*)=10,61mM.
20°,3	0,055	9,29	9,29
21°,5	0,045	8,30	8,30
22°,5	0,039	7,46	7,48
24°,7	0,029	5,72	5,66
25°,3	0,023	5,22	5.17
26°,6	0 016	4,09	4,10
27°,3	0,013	3,55	3,52
28°,4	0,007	2,62	2,61
28°,9	0,0[illegible]6	2,22	2,20
29°,3		1,88	1,87
29°,7		1,48	1,54
30°,2		1,00	1,13
30°,4		0,74	0,96
30°,5		0,62	0,88
30°,6		0,52	0,79

Till 30° the observations may be represented by the formula

$$H = 26{,}04 - 0{,}825\, t$$

by means of which the fourth column has been calculated. As the temperatures have not been read further than in tenths of a degree, differences of $\frac{0{,}0825}{2}$ between the observed and calculated H are possible; in two cases only this difference has been exceeded below 30⁰, what we may however ascribe to an experimental error.

Above 29⁰ the corrections become incertain; as they are however very small and reach zero at the critical point, I have put there $H = h$. It would perhaps not be quite unnecessary to make out whether a correction due to compression by gravity must be taken into account or not.

Surface-energy. — We calculated this energy by means of the formula

$$\sigma = \frac{1}{2}\, g\, H\, (\rho_l - \rho_v)\, r_1.$$

AMAGAT 1) has determined the densities ρ_l and ρ_v till at a distance, from the critical temperature, of some tenths of a degree only. His critical point 31⁰,35, is not quite the same as mine; this however does not cause the least difficulty when we compare densities and capillary ascensions observed, not at the same absolute temperature, but at the same distance of the corresponding critical one; or, what is identical, at the same *reduced* temperature 2).

CAILLETET and MATHIAS 3) have given parabolic interpolation-formulae for the densities of liquids and saturated vapours; according to these formulae we should have

$$\rho_l - \rho_v = k \sqrt{1 - m}.$$

And VAN DER WAALS 4) has shown that this relation

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1) Journ. de Phys., 3e sér., 1, p. 297, 1892.

2) If τ represents the distance from the critical point, and m the reduced temperature, we have between τ and m the relation

$$1 - m = 1 - \frac{T}{T_c} = \frac{\tau}{T_c}$$

T_c being the absolute temperature: 273⁰,3 + 31⁰,35 as found by AMAGAT, 273⁰,3 + 31⁰,0 in my experiments. The values of m corresponding to a same value of τ, are thus for densities and ascensions nearly quite indentical.

3) Journ. de Phys., 2e sér., 5, 1886.

4) *Thermodynamical theory.* The very thing demonstrated by VAN DER WAALS reads thus

$$V_v - V_c = \alpha\,(1 - m) + \beta \sqrt{1 - m}$$
$$V_l - V^c = \alpha\,(1 - m) - \beta \sqrt{1 - m}$$

must be satisfied at least very near the critical temperature.

In order to submit this first theoretical result to experimental verification I have calculated, from AMAGAT's densities, the values of the quotient $\frac{\triangle \log (\rho_l - \rho_v)}{\triangle \log (1 - m)}$, which, according to CAILLETET and MATHIAS must be constant and equal to 0,5, and would reach this value for $m = 1$, according to VAN DER WAALS.

$\tau = 0^0,1$	$1 - m = 0,00033$	$\rho_l - \rho_a = 0,075$	$\frac{\triangle \log (\rho_l - \rho_v)}{\triangle \log (1 - m)} = 0,521$
0°,35	0,00115	0,144	0,468
0°,85	0,00279	0,218	0,414
1⁰,35	0,0044	0,264	0,386
2⁰,35	0,0077	0,327	0,357
3⁰,35	0,0110	0,371	0,336
4⁰,35	0,0143	0,405	0,356
5⁰,35	0,0176	0,436	0,356
6⁰,35	0,0209	0,463	0,351
7⁰,35	0,0241	0,489	0,374
8⁰,35	0,0274	0,514	0,391
9⁰,35	0.0307	0,535	0,354
10⁰,35	0,0340	0,556	0,379
11⁰,35	0,0373	0,575	0,383

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and accordingly

$$V_v - V_l = 2\beta \sqrt{1 - m};$$

but thence

$$\rho_v = \frac{1}{V_c + \alpha (1 - m) + \beta \sqrt{1 - m}} = \rho_c - \rho_c^2 (\alpha - \rho_c \beta^2)(1 - m) - \beta \rho_c^2 \sqrt{1 - m}$$

$$\rho_l = \frac{1}{V_c + \alpha (1 - m) - \beta \sqrt{1 - m}} = \rho_c - \rho_c^2 (\alpha - \rho_c \beta^2)(1 - m) + \beta \rho_c^2 \sqrt{1 - m}$$

so

$$\rho_l - \rho_v = 2 \beta \rho_c^2 \sqrt{1 - m}.$$

Column 4 shows immediately that the formula of CAILLETET and MATHIAS does not well represent the experiments, for carbonic acid at least. Till 1° from the critical temperature the quotient $\frac{d \log (\rho_l - \rho_v)}{d \log (1 - m)}$ remains sensibly constant, mean value $= 0,367$, and the experiments can therefore be represented well by

$$\rho_l - \rho_v = \mathrm{A}\,(1 - m)^{0,367}$$

A being a constant.

From $\tau = \pm 1^0$ begins a sensible increase of the quotient $\frac{d \log (\rho_l - \rho_v)}{d \log (1 - m)}$, as required by the theory of VAN DER WAALS, and the last value 0,521 comes very near the theoretical one.

Let us now calculate the surface energy; the H has been deduced by graphical interpolation from my observations.

$1 - m = 0,00033$	$\mathrm{H} = 0,13$ mM.	$\sigma = 0,0021$	$\frac{\triangle \log \sigma}{\triangle \log (1 - m)} = 1,512$
0,00115	0,45	0,014	1,413
0,00279	1,04	0,049	1,248
0,0044	1,53	0,087	1,216
0,0077	2,42	0,171	1,187
0,0110	3,25	0,261	1,198
0,0143	4,07	0,357	1,242
0,0176	4,89	0,461	1,256
0,0209	5,71	0,572	1,291
0,0241	6,53	0,691	1,290
0,0274	7,35	0,817	1,318
0,0307	8,17	0,946	1,321
0,0340	8,99	1,082	1,341
0,0373	9,82	1,224	

We see that the quotient $\frac{d \log \sigma}{d \log (1 - m)}$ decreases till $\tau = \pm 2^{0}$ and then increases again. The last value 1,512 agrees again with the theoretical limit value 1,5.

Critical remarks. — When we examine sharply the conclusions arrived at, we must confess that the agreement found between theory and experiments has indeed not yet been proved.

For when we consider this first result, that the value of $\frac{d \log (\rho_l - \rho_v)}{d \log (1 - m)}$, obtained very near the critical temperature, is 0,521, while VAN DER WAALS deduced 0,5 from his equation of state, we see in it the expression of the fact that the density-curves have in the critical point a contact of the second order with their common tangent. The densities however used in our calculations, are not those observed by AMAGAT, but values deduced by graphical interpolation from the observed ones, in such a way that a curve was traced as near as possible to the observed points, and tangent to the ordinate of the critical point. And as we know that generally a curve has with every tangent a contact of the second order, we must confess that the obtained result, though it may really be contained in the experiments, is nevertheless a consequence of the manner of interpolating.

As for $\frac{d \log \sigma}{d \log (1 - m)}$, here also we could almost assert that agreement between theory and experiments would be found.

$$\frac{d \log \sigma}{d \log (1 - m)} = \frac{d \log \mathrm{H}}{d \log (1 - m)} + \frac{d \log (\rho_l - \rho_v)}{d \log (1 - m)}.$$

We have already seen that the limit-value of the last term is 0,5; and it appears from all experiments that the tangent to the H-curve in the critical point, may be represented by an equation $y = a(1 - m)$. As now $\frac{d \log y}{d \log (1 - m)} = 1$, we have also $\frac{d \log \mathrm{H}}{d \log (1 - m)} = 1$ at the critical temperature. So the limit-value 1,5 is a consequence of it.

This verification would therefore be satisfying only then when it was founded quite on observed densities; these observed values however I have nowhere found.