Such phenomena *may* be caused by refraction, whereas hitherto the only possible explanation was sought in the assumption of tremendous velocities in the line of vision.

The foregoing considerations may suffice to show that anomalous dispersion naturally accounts for a great number of solar phenomena. At any rate no future theory of the sun can ignore the laws of refraction.

Physics. — "*On the critical isothermal line and the densities of saturated vapour and liquid in isopentane and carbon dioxide.*" By Dr. J. E. VERSCHAFFELT (Communication N°. 55 from the Physical Laboraty at Leiden by Prof. H. KAMERLINGH ONNES).

(Read March 31, 1900).

To be able to deduce from my researches on the capillary ascensions near the critical temperature [1]) the surface tension I laid down the empiric formula:

$$\varrho_l - \varrho_v = 0,243 \, (1 - m)^{0,367}$$

which fairly well represents the densities of liquid ϱ_l and vapour ϱ_v of carbon dioxide at the absolute temperature T and the reduced temperature $m = \dfrac{T}{T_k}$ given by AMAGAT. This is not the case for the temperatures $\tau = 0°,1$, $\tau = 0°,35$, $\tau = 0°,85$, (supposing $\tau = T_k - T$) in which

$$\frac{\Delta \, log \, (\varrho_l - \varrho_v)}{\Delta \, log \, \tau} = 0,521 \quad \text{between } \tau = 0°,1 \text{ and } 0°,35$$

$$0,468 \quad » \quad \tau = 0°,35 \text{ » } 0°,85$$

(see Comm. N°. 28 p. 12). In order to represent the interpolation-curve given by AMAGAT by my formula, it would in this region be necessary to raise the exponent of $(1 - m)$ in this formula from 0.367 to for instance 0 5, the value occurring in the formula $\varrho_l - \varrho_v = A \sqrt{(1-m)}$, which has been deduced theoretically by VAN DER WAALS, and given empirically by CAILLETET and MATHIAS.

This deviation might as remarked in Communication N°. 28, be caused by the fact that AMAGAT, without giving a satisfactory experimental proof for it, has rounded off his interpolation-curve

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[1]) Comm. from the Phys Lab. at Leiden N°. 28, Dr. J. E. VERSCHAFFELT. Measurements on the capillary ascension of liquefied carbon dioxide near the critical temperature.

towards the critical state with a parabola of the second degree. In the very accurate determinations of density by SYDNEY YOUNG, to which no corrections by interpolation have been applied and for which I have computed a formula of the same form as the one mentioned above viz.

$$\varrho_l - \varrho_v = 0,11058 \ \tau^{0,3434}$$

the agreement between observation and calculation appears to exist even at the highest temperatures ($\tau = 0°,4$).

$$\frac{\Delta \ log \ (\varrho_l - \varrho_v)}{\Delta \ log \ \tau} \quad is \qquad between \quad \begin{array}{l} \tau = 1°,8 \ and \ 0°,8 \ still \ 0,344 \\ \tau = 0°,8 \ and \ 0°,4 \ still \ 0,337 \end{array}$$

while, according to the law of the corresponding states we might predict already at $\tau = 1°,5$ a distinct increase from the above-mentioned deviation in the case of the interpolation-curve of carbon dioxide.

Therefore for the time being no *experimental* proofs can be given for the supposition, that up to the immediate neighbourhood of the critical state $\varrho_l - \varrho_v = A \ (1 - m)^{0,3434}$ would not hold instead of the theoretical formula $\varrho_l - \varrho_v = A \ (1 - m)^{\frac{1}{2}}$.

The table given here shows that my formula gives precisely the difference in density till about $\tau = 60°$. With lower temperatures the agreement diminishes.

T A B L E I.

τ	$(\varrho_l - \varrho_v)$ observ.	$(\varrho_l - \varrho_v)$ calculat.
0,4	0,0810	0,0807
0,8	0,1023	0,1024
1,8	0,1351	0,1353
2,8	0,1567	0,1575
4,8	0,1889	0,1895
7,8	0,2240	0,2239
11,8	0,2591	0,2581
17,8	0,2982	0.2972
27,8	0,3477	0,3464
37,8	0,3862	0,3849
47,8	0,4169	0,4173
57,8	0,4443	0,4454
67,8	0,4680	0,4705

2. The relation deduced by VAN DER WAALS between the surface-tension σ and the reduced temperature m

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

is intimately connected with the form of the isothermals near the critical point, by means of which also the formula for the densities of liquid and vapour (with the aid of the MAXWELL-CLAUSIUS theorem) must be determined.

It now appears that in the place of the exponent $1/2$ in the difference of liquid and vapour density a less simple fraction must be substituted. Hence as according to VAN DER WAALS' simple supposition the isothermal is a curve of the third degree, I have investigated whether the critical isothermal could not be expressed in an analogous way by means of a fractional exponent. The result I arrived at, was that the observations of S. YOUNG on the form of the critical isothermal of isopentane are well expressed by the formulae:

$$p = p_c - p_c \left(1 - \frac{v_c - b}{v - b}\right)^n, \quad \text{for} \quad v > v_c$$

and

$$p = p_c + p_c \left(\frac{v_c - b}{v - b} - 1\right)^n, \quad \text{for} \quad v < v_c;$$

in which $p_c = 32{,}92$ atm., $v_c = 4{,}266$ c.c. (specific volume), $b = 0{,}518$ c.c., and $n = 4{,}259$. The following table shows that these formulae are in good harmony with the observations:

T A B L E II.

v	p (observ.)	p (calcul.)
19,41	19,99	20,06
16,91	21,95	21,99
14,40	24,13	24,27
11,91	26,84	26,86
9,440	29,69	29,65
4,505	32,92	32,92
3,160	33,70	33,73
3,050	34,39	34,35
2,939	35,49	35,56
2,829	37,49	37,32
2,718	40,51	40,37
2,608	45,49	45,27
2,497	53,51	53,58
2,431	60,59	60,42
2,394	65,24	65,60
2,361	70,63	70,87

From the formula given for $v > v_c$ it follows that for very great volumes $pv = 525,5$, from which $R = 1,140$, in good harmony with the value 1,138 found by applying AVOGRADO's law as holding for the limit [1]).

In order to know whether my formulae give also a sufficient approximation for very high pressures, I have calculated the critical isothermal from AMAGAT's system of isothermals for carbon dioxide. As critical temperature I found $31°,4$ C., hence $p_c = 73,6$ atm.; for v_c I took the value 0.00424 (the normal volume being chosen as unit), computed from the critical density 0.464. The following table shows that if $n = 4$ and $b = 0,00045$, my formulae well represent the observations up to pressures of about 800 atm. The third column gives the pressures I have computed from the volumes observed, and the fourth column gives the volumes computed from the pressure observed.

T A B L E III.

p	v	p (calcul)	v (calcul.)
1000	0,001752	1055	0,001764
950	1767	989	1776
900	1782	927	1789
850	1799	864	1803
800	1815	808	1817
750	1832	752	1835
700	1847	709	1850
650	1864	659	1868
600	1887	603	1888
550	1909	552	1910
500	1934	504	1936
450	1965	448,5	1964
400	1998,	397,3	1996
350	2037	346,7	2034
300	2087	294,3	2081
275	2115	268,5	2108
250	2148	242,9	2139
225	2182	220,3	2175
200	2220	198,6	2217

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[1]) Using the theoretical normal density for hydrogen
$0,0000S955 \times 1\,00059 = 0,00008961$
and the molecular weight of $C_5 H_{12} = 71\,S2$ (Comp Comm from the Leiden laboratory N°. 47 page 12)
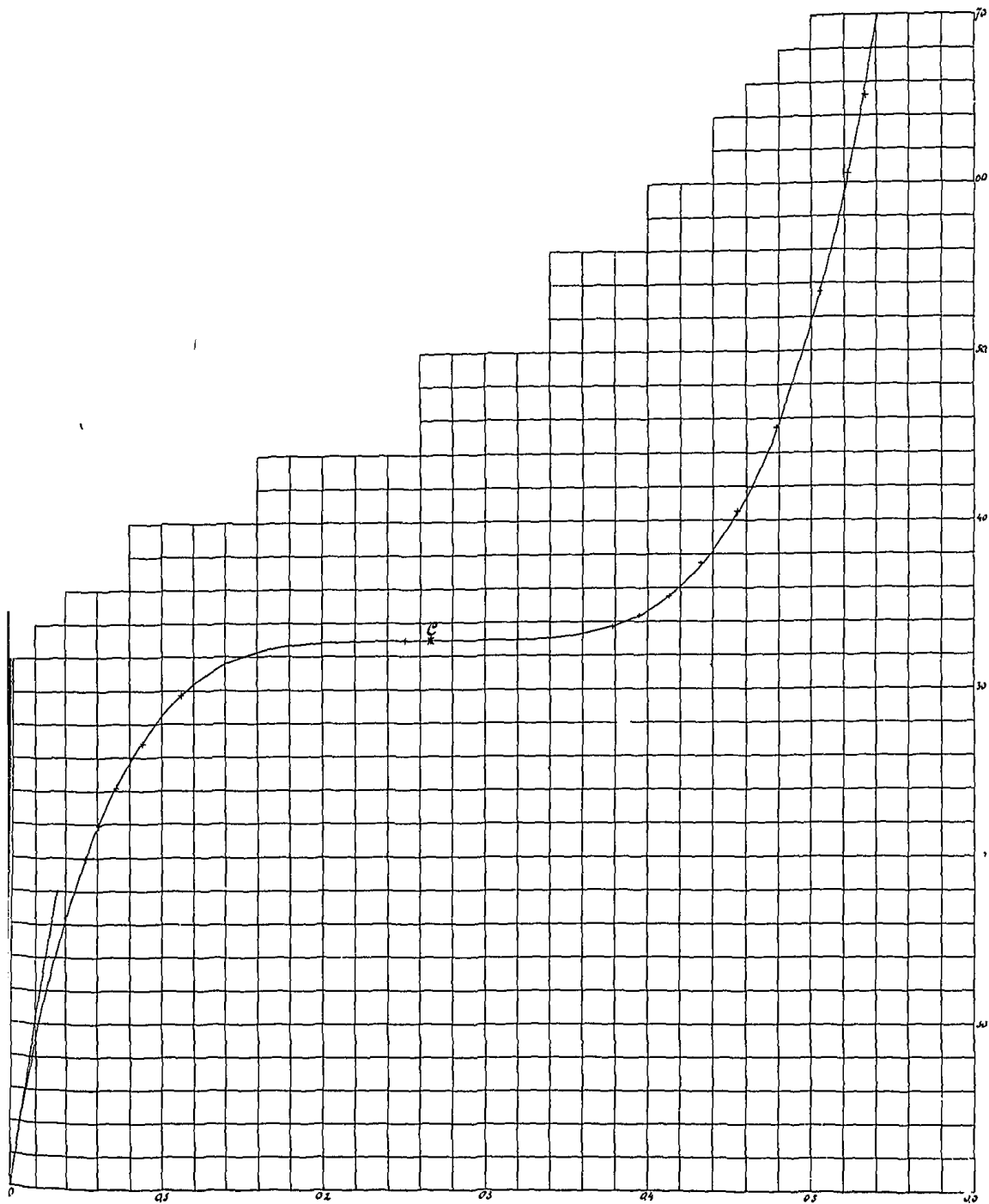
43

p	v	p (calcul)	v (calcul.)
175	0,002263	177,6	0,002269
150	2333	151,0	2336
125	2432	124,6	2430
100	2600	98,7	2587
76,30	3090	76,25	3086
74,50	3283	74,57	3295
73,75	3573	73,76	3576
73,26	547	73,34	558
72,37	630	72,46	637
71,42	682	71,62	693
69,50	771	69,76	782
67,57	850	67,83	861
64,63	968	64,72	972
59,71	0,01156	59,74	0,01157
54,77	1356	54,83	1359
49,81	1584	49,88	1588
44,84	1856	44,85	1856
39,86	2187	39,86	2186

3. The formulae I have found for the critical isothermals are purely empirical. I was led to using formulae of the form given above by the remark that it was possible to find such a value of b that the critical isothermal, drawn in a diagram with p as axis of ordinates and $\dfrac{1}{v-b}$ as axis of abscissae showed a centre of symmetry in the critical point. In the annexed figure, representing the critical isothermals of isopentane, this symmetry is very conspicuous.

The marks represent the observations, the line drawn represents my formula.

It may be seen that only in a very forced way a division of the pressure into a thermodynamical and a cohesion pressure can be deduced from my formula, which division is the basis of van der Waals' theory. If therefore my formulae have a theoretical meaning, this seems to be based on a principle somewhat different from van der Waals' equation of state; I did however not succeed in deducing such a principle.

Dr J. E. VERSCHAFFELT, „On the critical isothermal line and the densities of saturated vapour and liquid in isopentane and carbon dioxide."