**Physics.** — Dr. H. KAMERLINGH ONNES: *"On differences of density in the neighbourhood of the critical state arising from differences of temperatu e."* (Appendix to Communication N°. 68 from the Physical Laboratory at Leiden).

§ 1. At the former meeting I have demonstrated (Communication N°. 68) that the deviations from VAN DER WAALS' theory mentioned by DE HEEN, are not to be found when his experiments are repeated with pure carbon dioxide. From which I derived that systematical corrections must be applied to his results. Moreover I have proved experimentally that DE HEEN has wrongly left out of consideration differences of temperature resulting from adiabatic processes.

Other and perhaps very important differences of temperature may have arisen from DE HEEN's method of heating, as I briefly mentioned in § 3. As long as there are no proofs to the contrary we must consider that they have really existed. If other sources of errors could not be undoubtedly demonstrated, as has been done in Communication N°. 68, and if not small differences of pressure, which may have remained, might have had a similar influence as the differences of temperature meant here, we would be fully justified in ascribing entirely to them the deviations found by DE HEEN. For in the different experiments these deviations are related in a manner such as we should expect if the temperature in the upper part of the apparatus was higher than in the lower part, in agreement with the supposition laid down in § 2 1. c. It seemed to me desirable to explain here more in detail that this was the case, especially because with other experiments on the critical state, attention must be paid to deviations of the same kind, even when they are reduced to much smaller dimensions by the precautions of the observer.

From AMAGAT's observations in the neighbourhood of the critical state plotted in a diagram with regard to density and pressure the densities at intermediate temperatures are easily found by interpolation with the coefficients of pressure. In fig. 3 at ∂_t (the density at the temperature t) as abscissa I have plotted as ordinates ∂ itself and also ∂_{t+1} and ∂_{t-1},
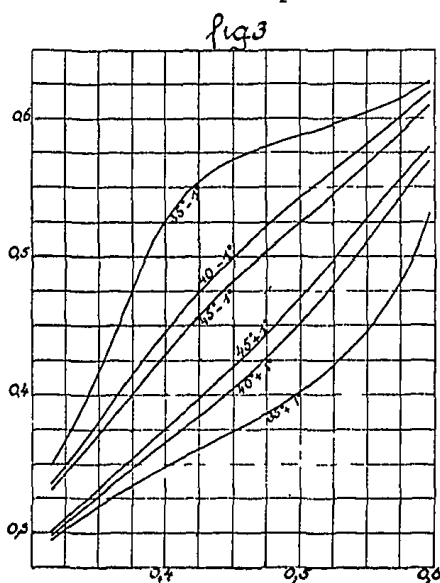
the values which under the same pressure are related to temperatures which are situated either 1 deg. C. higher or 1 deg. C. lower than t. The isothermal of density ∂_t gives in this figure the same line for all values of t (it is drawn as a dotted line at an angle of 45°). Two curves ∂_{t+1} and ∂_{t-1} belong to each temperature t and indicate by the difference of their ordinates from that of the line drawn at an angle of 45° the variation of density for 1 deg. C. difference of temperature from the density ∂_t at $t°$. In this way the deviations for 1 deg. C. at 35° C., 40° C. and 45° C. are each represented by two of these curves of deviation.

This figure shows very clearly that at some densities even small differences in temperature at 35° C. may lead to important variations in density. For the correction to the experiments treated in Communication N°. 68 § 2 it gives much larger values, than those derived there by means of a mean coefficient of expansion. The latter had wrongly been calculated from the difference in density between two limits of temperatures within which the coefficient of density variation has a maximum. The use of a mean coefficient of expansion is only allowed within narrow limits of temperature in that case. However in judging DE HEEN's experiments, I have attached small value to this correction. The measurement of the difference of temperature, from which it must be calculated, left much to be desired in my preliminary determinations; (the reason why further determinations were not made has been explained in § 1 of Communication 68). During the experiments one of the wires of the thermo-element was broken, so that a correction must be applied to the differences of temperature measured. This is not of any account for the measurement of the variation of the difference in temperature (Comp. § 3) of the two reservoirs caused by the opening of the cock, but yet leaves uncertain this difference in temperature itself. And the chief arguments for the refutation of DE HEEN's hypothesis was that I found the densities in the upper reservoir only slightly smaller than those in the lower, although it was certain that the former had a somewhat higher temperature than the latter.

§ 2. With very small differences of temperature the difference of the mean densities in two parts of a cylinder in which the temperature varies with the height according to a given law (e.g. linearly) can easily be calculated. In a case such as the experiments of DE HEEN it seems to me probable that we may put:

$$t = t_0 + 2\lambda h,$$

in which t_0 stands for the temperature at a given height, for instance that of the cock of his apparatus, and h for the height of the layer with temperature t, above that given height.

If ∂_{pt} represents the density at a given pressure and temperature then we may put, at very small differences of temperature

$$\partial_{pt} = \partial_{pt_0} + \Delta\,(t - t_0),$$

in which $\Delta = \dfrac{d\partial_p}{dt}$ can be deduced from fig. 3. If the upper end of the upper reservoir stands at h_s and the lower end of the lower reservoir at h_i, then the mean density ∂_s in the upper reservoir and ∂_i in the lower reservoir is:

$$\left.\begin{aligned}
\partial_s &= \partial_{pt_0} + \Delta\,\lambda\,h_s \\
\partial_\iota &= \partial_{pt_0} + \Delta\,\lambda\,h_i
\end{aligned}\right\} \quad \ldots \ldots \ldots (1)$$

In the case of DE HEEN, putting $h_s - h_i = 1$, λ gives the difference between the temperature at the middle of the upper and of the lower reservoirs.

For the mean density ∂_m in the whole reservoir from

$$\partial_s h_s - \partial_i h_i = \partial_m$$

we find

$$\partial_m = \partial_{pt_0} + \Delta\,\lambda\,(h_s + h_i). \quad \ldots \ldots \ldots (2)$$

In DE HEEN's first series of experiments, neglecting the dimensions of the cock we find

$$h_s = 0,5 \quad h_i = -0,5 \quad \partial_m = \partial_{pt_0}$$

and so what DE HEEN gives in this series as the densities of vapour ∂_{dl} and of liquid ∂_{vl} we find to be

$$\left.\begin{aligned}
\partial_{dl} &= \partial_m + 0,5\,\Delta\,\lambda \\
\partial_{vI} &= \partial_m - 0,5\,\Delta\,\lambda
\end{aligned}\right\} \quad \ldots \ldots \ldots (3)$$

and the difference of the so-called vapour and liquid density at the same ∂_m

$$\partial_{vI} - \partial_{dI} = -\,\Delta\,\lambda. \quad \ldots \ldots \ldots (3^a)$$

In DE HEEN's second series of experiments a difference must be made between a determination of what he calls a vapour density and what he calls a liquid density. (Comp. Communication N^0. 68).

In the first case we must put $h_s = 0,229$, $h_i = -0,771$ and according to (2)

$$\partial_m^{(d)} = \partial_{t0}^{(d)} + \Delta \lambda (0,229-0,771)$$

in the second case

$$\partial_m^{(v)} = \partial_{t0}^{(v)} + \Delta \lambda (0,845-0,155).$$

So that by means of (1) we find for the vapour density ∂_{dII} and the liquid density ∂_{vII} given by DE HEEN in the series

$$\left.\begin{array}{l} \partial_{dII} = \partial_m^{(d)} + 0,771 \, \Delta \lambda \\[2em] \partial_{vII} = \partial_m^{(v)} - 0,845 \, \Delta \lambda \end{array}\right\} \quad \ldots \ldots \ldots (4)$$

or also for the same value of $\partial_m^{(d)}$ and $\partial_m^{(v)}$

$$\partial_{vII} - \partial_{dII} = -1,62 \, \Delta \lambda. \quad \ldots \ldots \ldots (4^a)$$

In the two series the same value will have to be put for λ, and Δ will also be the same at the same ∂; hence it follows from (3^a) and (4^a) that the deviations, which originate in λ, will be much greater in the second series than in the first.

DE HEEN found for the experiment treated in Communication N^0. 68, § 2 and § 3 in the first series

$$\partial_{vI} - \partial_{dI} = 0,088$$

in the second series, where another source of error occurred (comp. Communication N^0. 68).
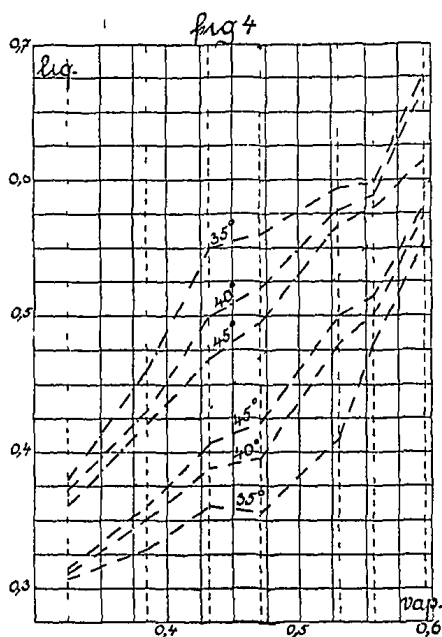
$$\partial_{vII} - \partial_{dII} = 0,190.$$

From the combined deviations at 35°, 40° and 45° C. in DE HEEN's second series according to the table considered in Communication N^0. 68, if we desired to attribute the deviations found *exclusively* to the differences in temperature considered now and if we equalise λ for all temperatures, I find $\lambda = 1°,35$. Here I have put the deviation for 1 deg. increase for Δ in the ∂_d equation, that for 1 deg. decrease in the ∂_v equation, both derived from fig. 3.

Then approximately we have

$$\partial_{d\,II} = \partial_m^{(d)} + \Delta$$

$$\partial_{v\,II} = \partial_m^{(v)} - \Delta$$

The so-called liquid densities and vapour densities of this series of DE HEEN (as in § 4 of Communication N°. 68) if drawn as ordinates against the mean-density as abscissa, must then give the same figure as fig. 3. From fig 4 may be seen that this is actually the case. This figure gives the curves for 35° C., 40° C. and 45° C. for DE HEEN's experiments borrowed from a drawing by VERSCHAFFELT (comp. Communication N°. 68). Except for accidental errors the figure is in sufficient agreement with fig. 3. The whole system of deviations from DE HEEN's experiments agrees therefore with that which would result from the supposed distribution of temperature.

§ 3. Also the increase of the vapour density with regard to the mean density in DE HEEN's experiments below the critical temperature (see fig. 1 of Communication N°. 68) is in correspondence with the supposition that the temperature increases in the direction from the lower reservoir to the upper. In fig. 2 of the same, calculated from AMAGAT's observations supposing that in the two reservoirs of DE HEEN the temperature was everywhere the same, this rise of the curve on the vapour side, as long as the liquid surface does not enter into the upper reservoir, does not of course occur. If however the temperature in the two reservoirs increases in the said direction the temperature at the height of the liquid surface in the lower reservoir will be higher at a greater than at a smaller mean density. The maximum vapour tension increases therefore and also the density in the upper reservoir. This will be even more the case with temperatures coming nearer to the critical than with lower temperatures. This peculiarity is also found in the deviations of DE HEEN's results.