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Physics. — Prof. H. KAMERLINGH ONNES: "*On DE HEEN'S experiments about the critical state.*" (Communication N^o. 68 from the physical laboratory at Leiden).

§ 1. *Purpose of this communication.* Experiments have been repeatedly described which were alleged to disprove the notion of the continuity of the liquid and gaseous states according to VAN DER WAALS' theory. They especially were said to deny that a simple substance should have only one critical temperature, one critical pressure and one critical volume, that it should possess at a given pressure and temperature above the critical temperature one density only; and that below the critical temperature it can present stable co-existing phases in equilibrium for each temperature only at two definite densities.

Each time however it was possible to point out circumstances which had been overlooked in the experiments. If the experiments mentioned were repeated with due regard to the necessary precautions, they proved to confirm VAN DER WAALS' views.

It required much care to find out the circumstances to which we must attribute the deviations observed in GALITZINE'S experiments. At the Leiden laboratory where VAN DER WAALS' theory was made the starting point of several investigations, KUENEN has undertaken this difficult and lengthy work. He succeeded (Comm. N^o. 11 May and June '94) in explaining experimentally the phenomena observed by GALITZINE by the influence of admixtures, impurities which amounted to only a few tenthousandths of the substance, considered pure. By this elaborate research we not only considered GALITZINE'S views to be refuted but also ideas so nearly related to them as those of DE HEEN. At least it seemed decided, that henceforth no value might be attached to researches on the critical state with simple substances, unless it was proved that even such small impurities as occurred in GALITZINE'S experiments were avoided.

KUENEN'S experiments failed however to convince DE HEEN that his objections against VAN DER WAALS' theory were not justifiable; nor did it make him aware of the necessity to bestow as much care on the purifying of the experimental substance as we are wont to do. On the contrary, in 1896¹⁾ DE HEEN has published new experiments, made with carbon dioxide, again without stating anything concerning precautions taken for its purification.

According to him these experiments would show:

¹⁾ Bulletin de l'Institut de physique de l'Université de Liège, deuxième fascicule (Bull. de l'Ac. Roy. de Belgique 3^e Sér. t. XXXI, '96).

that a definite critical density, of which the existence has hitherto been accepted, is an entirely fictitious quantity, that in reality there are two critical densities, 1st. the critical density of the liquid, 0.640 for carbon dioxide; 2nd. the critical density of the gas, 0.298 for carbon dioxide, and that the quantity hitherto measured as critical density is the mean of these two limiting densities.

Shortly afterwards a visit of DE HEEN to Leiden offered an opportunity for a discussion in which I pointed out, that very small deviations in temperature, pressure and composition near the critical state can lead to great variations in density. My remark that in DE HEEN's experiment the carbon dioxide had not been perfectly pure was not contradicted. Whereas to me this circumstance seemed very important, DE HEEN did not set much value upon it.

It seemed that the controversy could be solved by repeating at the Leiden laboratory DE HEEN's measurements in his own apparatus with carbon dioxide of the same purity as it is used with us for similar experiments. During the repetition of these measurements other precautions which seemed desirable to me might also be taken. I found Dr. J. E. VERSCHAFFELT, then assistant at the Leiden Laboratory, willing to undertake the work and Prof. DE HEEN was kind enough to send to Leiden the "analysateur de l'état critique". But when we began working the apparatus, it proved unfit for experiments with very pure carbon dioxide. For the liquefied gas came into contact with the packing. This was made of leather soaked with wax or grease, which substances dissolve in the liquid carbon dioxide so much that they can even be distinctly smelt when the liquid is drawn off. The packing boxes did not allow us to substitute for the leather packing, cork or lead. Even if the carbon dioxide before being admitted into the apparatus had been as pure as we desired it, the results obtained would not have related to pure carbon dioxide. Besides the introduction of new packing boxes, the apparatus called for radical modifications in order to allow us to inquire whether, even though it remained impossible to verify the homogeneity of the phases, the two quantities of the substance, of which DE HEEN in each case compares the densities, have indeed the same temperature and pressure. DE HEEN supposes that this is true, but the construction of the apparatus used by him does not permit of a proof.

Hence we could only profit from the presence of the apparatus at Leiden by studying some of its peculiarities, and the matter was not further entered into.

In '97 DE HEEN thought that he found a proof of the exactness

of his observations in those of AMAGAT. He derived from AMAGAT's experiments that there are two densities near the critical point, which are in the ratio of 1 : 2 and he wrote: J'ai du reste la conviction que la théorie que je viens de soutenir ne commencera à se généraliser que lorsque les expériences — namely those with the analyseur de l'état critique — auront été répétés un grand nombre de fois par plusieurs physiciens. Ce n'est que dans ces conditions qu'on peut porter atteinte à des convictions — the existence of one critical state — ayant poussé de si profondes racines.

The result of a careful repetition of those experiments could however not be doubtful in our opinion. For who ever wishes to repeat DE HEEN's measurements of density, will want to arrange the work so that it will be possible to verify the homogeneity of each of the phases, and to measure accurately small differences in temperature, pressure and composition of the phases to be compared, in order to calculate by them corresponding corrections. It would also be desirable to apply even now similar corrections to the numbers given by DE HEEN, in order to arrive thereby at the true results of his researches. But as DE HEEN has paid no attention to the data for the determination of these corrections, this is not possible. We nevertheless can form an idea of their general character. And so Dr. VERSCHAFFELT and I in going over DE HEEN's experiments were soon convinced that these, however improbable this may seem to him, would agree with VAN DER WAALS' theory within the limits of the errors of observation after the necessary corrections had been applied.

In order to show moreover experimentally that such corrections must be actually applied an apparatus — chiefly consisting of two reservoirs connected by a cock, from each of which the contents could be collected by a small cock — was constructed of several pieces available in the laboratory, with which we intended to repeat some of DE HEEN's measurements with the necessary precautions.

When Dr. VERSCHAFFELT left Leiden, I have myself devoted some time to preliminary observations with an improved apparatus better answering the purpose. Among other things I had introduced a thermo-element in each of the reservoirs mentioned.

During these preliminary measurements nothing was observed (see following sections) that could point to the important deviations which were derived by DE HEEN from the experiments chosen for repetition, and it was confirmed that it was necessary to apply corrections to the densities given by him.

Hence a continuation of this repetition of DE HEEN's experiments

appeared to be only useful in that it exhibited by means of his results the amount of deviation which can be found, whenever we are not guided by the theory of the mixtures and of the adiabatic variations of state in measurements with compressed gases in the neighbourhood of the critical state. The most important point in this question, namely the influence of small admixtures on the phenomena in the neighbourhood of the critical state, will be illustrated by other investigations which are being made here and as I hope even better than could be done by the measurements mentioned.

More urgent work obliged us to leave undone the measurements in which the conditions for the deviations given by DE HEEN were intentionally realized, and the apparatus was taken to pieces. Nor did my time allow me to make further investigations in connection with DE HEEN's experiments. In the "Mathematische Encyclopædie" I hope to return to some questions relative to the theory of the critical state. And what could be remarked on DE HEEN's experiments, seemed to me after I had tried to write down something on them not sufficiently interesting for a paper.

But a few days before the last meeting I received DE HEEN's paper „les légendes du point critique", in which he expresses in a friendly tone his earnest wish that I should now communicate publicly my opinion on his work.

I avail myself of this opportunity to express to Prof. DE HEEN in return my feelings of friendship and respect. I have tried to satisfy his request by what I have said above and by explaining it more in detail in the following sections

2. *Investigation of one of the systematic deviations.* KUENEN has already pointed out how unsatisfactory is a refutation of theories so little defined as those of DE HEEN. The refutation of the results derived by DE HEEN from his measurements by repeating them is as little inviting. Since it is a repetition we are bound to a method of working deviating much from that, which we should think it necessary to follow in similar investigations. Moreover what we call taking precautions may be considered by DE HEEN as sacrificing an artifice, lastly to attain a moderate accuracy in measurements with compressed gases, operations are necessary which require much time and care. If therefore in the repetition of DE HEEN's experiments a high degree of accuracy was required I would not have undertaken it. But a determination of density to within 3 percent is sufficient, as the deviations between DE HEEN's results and those which

can be derived from the laws generally accepted, even at several degrees' distance from the critical temperature, amounted in some cases to 30 and 40 percent¹⁾. Also for the experiments to be considered below, the deviation is large enough to be refuted by measurements of the accuracy mentioned. Besides it is a favourable circumstance that all the deviations are connected systematically. It is easy to see this from DE HEEN's table. (l. c. p. 386). If therefore one of the important deviations mentioned by DE HEEN can, by the repetition of the experiment from which it was derived, be reduced to zero within the limits of the errors of observations, this involves the refutation of all the others.

Although I will not dwell on the theoretical considerations refuted by KUENEN I must shortly explain which is the chief point in the experiment to be repeated.

DE HEEN assumes the existence of so-called liquidogen and gasogen molecules. The former would only be decomposed far above the critical temperature. If we succeed in filling a space near or just above the critical temperature entirely with liquidogen molecules then the substance enclosed therein will have one of the limiting densities given by DE HEEN for the critical state; if we succeed in doing the same for the gasogen molecules, the second limiting density will be observed. Above the critical temperature, mixtures of those kinds of molecules can be made in all proportions. If a space filled with liquidogen molecules is in contact with an other containing gasogen molecules, so that mutual diffusion can take place, the liquidogen and the gasogen molecules will be mixed. Only when they have been completely mixed — and so after some time — the difference between the densities in these two spaces disappears.

DE HEEN's analysateur de l'état critique renders it possible by means of a cock to divide the volume occupied by a substance into two parts at a moment of pressure equilibrium and in this way if one space contains chiefly liquidogen, and the other chiefly gasogen molecules, to prevent the mixing of these two. The substances in each of the two reservoirs mentioned in § 1, which are placed above each other and are separated by a cock, can moreover be separately collected by means of cocks made for this purpose. According to DE HEEN it would be possible by taking care that at first the lower reservoir should be filled chiefly with liquid, and the upper reservoir chiefly with vapour, to fill above the criti-

¹⁾ For instance, influences like those of gravitation (Comp. Comm. No. 17 KUENEN, May '95,) can be left out of account.

cal temperature one space chiefly with liquidogen, to other chiefly with gasogen molecules under the same pressure. At the same pressure and the same temperature different densities would then be found in the two spaces.

DE HEEN has not made clear, what could be learned better from the experiments with the "analysateur" than from the experiments with the tubes of GALITZINE.

For in the latter case the two phases, the one consisting chiefly of supposed liquidogen molecules, the other chiefly of supposed gasogen molecules, are heated separately, while the movable mercury thread which separates them is constantly yielding to the difference of pressure between the two phases, and indicates if the equilibrium is not attained, for which difference of pressure a correction is to be applied in the comparison of the densities.

As compared with this contrivance the making of a partition between the space where more liquidogen, and that where more gasogen molecules are supposed to be, by means of a cock which is only opened now and then, may be considered as a step backwards. In this way mixture by means of diffusion cannot be avoided so well, nor can the equilibrium of temperature and pressure be so well attained or accounted for. If DE HEEN had succeeded in separating perceptibly the liquidogen and the gasogen molecules, then they ought to have been observable certainly in GALITZINE's tubes, as indeed this physicist thought. KUENEN by his experiments has proved that this was not the case.

If discussion of DE HEEN's theses was primarily required then we might argue that everything derived by DE HEEN from the experiments with the "analysateur" has been à fortiori refuted by KUENEN's criticism of GALITZINE's arguments.

But our aim was to demonstrate by the repetition of DE HEEN's experiments with the necessary precautions, that they lead to other results than those given by DE HEEN. Like DE HEEN we used for this purpose two metal reservoirs separated by a cock.

I must still mention one point of difference between the „analysateur" and our apparatus meant in § 1. The reservoirs of our apparatus have an invariable volume. This is not the case with the „analysateur". In each of the cylindrical reservoirs of the "analysateur" a piston can be moved and these two pistons are so connected, that when they are moved the volume occupied by the substance in the two reservoirs together remains unaltered. By adjusting the pistons properly and by filling only one of the reservoirs, any suitable quantity of liquid can be admitted into the

apparatus, which may be distributed by means of the connecting cock over the total space of the two reservoirs, after which by re-adjusting the pistons the total space can be again divided into two parts of a desired ratio by means of the cock. And so it is easy to make a series of different measurements for different ratios with the same apparatus. It is also possible to alter the proportion of the two volumes during an experiment. It is obvious that the first mentioned speciality is useless in the repetition of a given experiment, it being moreover of little importance, as the desired filling can also be made in an other way, for instance by distillation, and as DE HEEN uses for the first series of experiments only one proportion and for the other only two extreme proportions. As will be seen, what might be attained by moving the piston during the experiment, is from DE HEEN's reasoning of no importance for the results to be obtained by repeating his experiment, or may be arrived at in another way.

After this digression we come to consider the experiment of DE HEEN which I had chosen for repetition. In this (Bulletin de l'Institut de Liège Deuxième fascicule p. 150) the pistons of the analysateur are placed so that the volumes of the two reservoirs are equal. Then the two reservoirs are filled at 10°C. with liquid carbon dioxide and the connecting cock is closed. The carbon dioxide from the upper reservoir is blown off, the connecting cock is opened, the carbon dioxide is allowed to fill the two reservoirs and to reach equilibrium, and then the apparatus is heated to 35°C. After the connecting cock is closed the contents of the two reservoirs are separately collected. For the density at 35°C. in the upper cylinder DE HEEN gives 0.456, for that in the lower cylinder 0.544, whereas according to VAN DER WAALS the densities of two quantities of pure carbon-dioxide, no matter how they are obtained, must be the same under the same pressure at 35°C.

The reason why this special experiment has been chosen for repetition is that it lies not too near the critical temperature and yet shows important deviations; also because according to AMAGAT's data the surface of the liquid in the apparatus at 28°C. stands very near the cock; and lastly and chiefly because in this case DE HEEN does not move the pistons of the "analysateur". For this reason it could be repeated with the apparatus described above, as the latter has two metal reservoirs of unvariable and almost equal volume with a connecting cock. And so the apparatus is for this experiment equivalent to that of DE HEEN.

Carbon dioxide was admitted into it which had been distilled at ordinary temperature over phosphorus pentoxide and boiled at a low temperature, and which in the liquid state had been into contact

with clean metal only. Before the carbon dioxide was admitted the apparatus had been evacuated by a BESSEL HAGEN'S air Auxiliary apparatus of which the volume had been measured. It was considered it possible to admit by distillation the exact weight of carbon dioxide into the two reservoirs with open connecting cock. It was taken that the liquid carbon dioxide was exclusively contained in the lower reservoir. During the heating namely, the temperature of the upper reservoir was kept a little above that of the lower reservoir so that below the critical temperature no liquid could distill from the lower reservoir into the upper reservoir. It seems that in this way better than by the method of the moving piston as followed by DE HEEN in his later experiments, certainty was obtained that at the beginning as little liquid as possible is in the upper reservoir.

The connecting cock was closed at 28° C., then the temperature was raised to 35° C. by streaming water of this temperature. During the heating the cock was opened six times for 4 seconds and after the heating another 6 times for 4 seconds at constant temperature. Several experiments had proved, that 4 seconds was a time long enough to secure equilibrium of pressure. In this time equilibrium of temperature was not yet attained, but it was not necessary with my apparatus to wait for it, the temperature could be determined by the thermo-element in both the two reservoirs separately, and so a correction could be applied. According to DE HEEN'S reasoning the liquidogen and the gasogen molecules in my experiment must have had less opportunity of escaping or returning by their diffusion, than with his own experiment, where the cock was left open while heating from 28° C. to 35° C. In my experiment the cock was closed at 34.°8 C. the ratio of the densities was $\frac{0.448}{0.426} = 1.052$. By applying the correction for the difference in temperature 0.8 deg. as given by the thermo-elements (the real difference was probably smaller) this ratio would become $\frac{0.448}{0.467} = 0.96$. For the permanent gas no correction was required as it amounted in the analysis of the original gas-phase to 0.00018 only and in the original liquid-phase to 0.00016 only.

And so only a small deviation was found becoming opposite in sign to that of DE HEEN by a correction of uncertain amount, which taking into account the errors of observation, would be expressed in DE HEEN'S language by the statement that the liquidogen and the gasogen molecules are the same.

A second experiment must be mentioned in which the con-

cock was left open during the heating from 28°C. to 35°C., heat being applied from above, and where I allowed 10 minutes for the attainment of equilibrium in the temperature and pressure. This period is probably too long to allow us to consider this experiment as a repetition of DE HEEN's, but certainly not sufficient for the two kinds of molecules to get mixed in a considerable degree through the narrow cock by diffusion according to our ordinary views. When the cock was closed at 35.4 C. the ratio of the densities was $\frac{0.448}{0.432} = 1.037$. By applying the correction for the difference of temperature of 1°.15C. as given by the thermo-elements, this proportion would become $\frac{0.448}{0.492}$ and by correction for the permanent gas, found at the analysis to be 0.002, $\frac{0.449}{0.494} = 0.91$.

Although as said in § 1 I attach no other importance to these numbers than that of preliminary observations, yet they are sufficient to regard DE HEEN's measurement, which gave the ratio $\frac{0.544}{0.456} = 1.19$, as disproved (especially by the first experiment).

Even if I suppose the error of observation in my densities to exceed 3 pCt., then DE HEEN's much larger deviation still remains disproved.

Nor can my proof be weakened by the fact that the differences of temperature were certainly over-estimated, and that with other less complete measurements of the same series which, as I have said already, were treated entirely as preliminary observations, deviations of the uncorrected densities were found which amounted even to more percents and which were in the sense of DE HEEN; on the contrary they showed, I think, that the errors which are likely to be made, tend towards the direction of the deviations found by DE HEEN.

And so DE HEEN's statement "ainsi se trouve mis hors de doute cette proposition tant contestée que nous avons émise depuis longtemps: La température et la pression ne suffissent pas toujours pour définir la densité d'un fluide" — is not in the least supported by his experiments.

§ 3. *Explanation of the deviations found above the critical temperature.* It is certainly remarkable that the differences given by DE HEEN which we have shown to be due to the neglect of corrections, are so considerable.

There is no objection for supposing that differences in temperature have remained e.g. in consequence of compression in the one reservoir and expansion in the other, which necessarily attend the transfer of substance from the lower into the upper reservoir, which moreover was very likely also warmer for other reasons.

I would be inclined however to ascribe the deviations partly to the presence of impurities. The carbon dioxide obtained from commercial cylinders, contains sometimes a few per cent of its volume of admixed air, besides traces of water vapour. DE HEEN has compressed it by means of a compression-pump, and it is known how difficult it is to keep a gas pure during this operation. Moreover it appeared necessary in DE HEEN's experiments in order to condense the carbon dioxide at 10° C in the apparatus to raise the pressure to 75 atmospheres, whereas the saturation pressure of carbon dioxide at that temperature amounts to only 45 atmospheres.

We have seen that the liquid carbon dioxide dissolves the oil and grease of the packing. In the gaseous phase the molecular pressure will decrease by the admixture of more volatile substances; in the liquid phase it will be increased by the less volatile admixtures. Owing to the large compressibility in the neighbourhood of the critical state, the densities belonging to a same external pressure may show considerable differences.

If the two phases of different composition are raised to a higher temperature the influence of the deviation in the molecular pressure will be diminished. And so the differences of density will be smaller. This is also the result obtained by DE HEEN.

In order to avoid as much as possible the diffusion of the liquid and gaseous molecules during the long time which is required to attain the equilibrium at a higher temperature, DE HEEN conducted these experiments in the following way:

„il suffit de porter l'appareil à une température peu supérieure à la température critique, par exemple 35° , puis de fermer la valve (the connecting cock) tout en continuant à chauffer jusqu'au point voulu. Lorsque celui-ci est réalisé on ouvre D , on laisse l'équilibre s'établir. Puis on recueille séparément l'acide renfermé dans les deux cylindres.”

From this it may be seen that the artifice of which we avail ourselves in heating to 35° C. has been borrowed from DE HEEN.

From the system of isothermals (pressure, volume) it may be seen at a glance that the pressure for the two phases with densities either side of the critical density will increase very differently on heating at constant volume, so that when the desired temperature

is attained, a considerable difference of pressure will exist between the two phases before the cock is opened. This causes on opening the cock a difference of temperature, which would prevent the equalization of densities from being completed when the process was purely adiabatic. With the slow transport of heat, which in reality takes place, equalization will be still retarded.

Before DE HEEN could therefore set any value upon the densities found after the closure of the cock, as belonging to a same temperature and pressure, he ought to have shown that the equilibrium of temperature had been obtained. With my apparatus treated in § 2 the process might be interrupted at any time, as soon as the equilibrium of pressure had once been attained, because the remaining difference of temperature could be determined and accounted for. But this was not so in the case of DE HEEN.

It is obvious that as the cock is left open during a shorter time, a greater difference of temperature will remain. The corrections to be applied will accordingly be the greater. In a series of observations, if the cock is opened in the same way every time, they will follow a systematic course, like the corrections for the small admixtures, if the carbon dioxide used was always of the same composition, and like any other correction, which belongs to an operation always performed in the same way e.g. the manner of heating.

Obviously larger corrections must be applied to DE HEEN's second series of experiments, which he performed in order to avoid diffusion, in the following way:

"Il faut donc amener les pistons dans la position (fig. 6) ou (fig. 7) — giving a definite ratio between the volumes of the reservoirs — à une température un peu inférieure au point critique, puis on ferme *D* et on continue à chauffer jusqu' à une température voulue. Pendant que la température s'élève on ouvre de temps en temps et rapidement¹⁾ le robinet *D*, de manière à permettre à la pression de s'équilibrer dans les deux cylindres, tout en empêchant les molécules liquidogéniques du cylindre inférieur de se diffuser dans le cylindre supérieur." —

Whereas in the experiment discussed in § 2 DE HEEN arrived at the two densities 0.456 and 0.544 or the ratio 1.19, he gives as results in the second series under almost the same circumstances the densities 0.360 and 0.550 and so a ratio of 1.44, where I found the theoretical ratio 1.00 sufficiently verified. And so in my

¹⁾ About 5 times, lasting 4 seconds each, as DE HEEN was kind enough to inform me.

opinion an extraordinary large correction must be applied to systematic errors.

Part of the systematic errors must be due to the shortness of the time during which the cock is opened. Near the critical point it is indeed an inefficient means for obtaining the desired equilibrium of pressure and temperature.

DE HEEN has been aware that when the cock was opened only, a difference in temperature could arise by the expansion of the substance in the lower reservoir. But it seems to have escaped his notice, that in the very neighbourhood of the critical state an adiabatic process is not at all favourable to equalization of pressure.

The process can be traced graphically by means of a diagram showing the isothermals and adiabatics near the critical point.

It will be sufficient to show its character. Hence it is allowable to simplify it and to trace the variations of two masses of the two phases, which are heated both at a constant volume, then are adiabatically brought to equilibrium of pressure, then again heated isometrically to a higher temperature, once more brought to equilibrium of pressure adiabatically etc. We neglect the modification undergone by each of the phases on account of the exchange of substance which takes place from the lower reservoir into the other.

In order to arrive at a definite diagram of the adiabatics and isothermals, we may for simplicity imagine it as derived from VAN DER WAALS' equation of state. Near the critical point the adiabatics coincide almost with the lines of constant volume, and so adiabatic equalization of the difference of pressure will hardly give a variation of the specific volume. The phases which first at equal temperature differed in pressure, after equalization of pressure differ so much in temperature, that the density is only slightly changed. The difference of pressure has been transformed into a difference of temperature almost equivalent with regard to the difference of density, and a difference of temperature with a slow transport of heat will in time not vanish when the cock is closed after a few seconds.

When the cock is opened for a short time this should be repeated very often in order to ensure the equilibrium of temperature.

This reasoning was confirmed by my observations with the elements. After having heated the apparatus from 28° C. to a closed cock to 35° C. and opening the cock according to DE HEEN'S method only 5 times for 4 seconds, I repeatedly found successive further openings of the cock and a renewed difference of temperature.

The observations have not been made accurately enough to set much value upon the numbers obtained, but they always tended to show a heating of the upper reservoir by the opening of the cock. (On an average $0^{\circ}.27$ C. in the experiment of § 2).

Besides the difference in the treatment of the cock, DE HEEN's second series of experiments is distinguished from the first by a second modification, which favours greater differences. Let us here consider only DE HEEN's two experiments mentioned above. In both cases the apparatus is heated from 10° C. to 35° C. and it contains a quantity of substance, which when distributed over the whole space, would show almost the critical density (according to current views). In both cases the apparatus is filled by first adjusting the pistons so that the total volume is exactly divided into two parts, and by then filling the one reservoir completely with liquid at 10° C. and distributing this quantity of substance over the two reservoirs.

But in the first series the apparatus is then heated without further operations. In the second series by readjusting the pistons all the substance is first brought below the cock, the apparatus is heated to a little below the critical temperature and then the piston is adjusted until a definite ratio between the space of the lower reservoir and of the upper reservoir is obtained. That ratio is $\frac{0.155}{0.845}$ when a determination of the density of liquid is wanted, $\frac{0.771}{0.229}$ when a determination of the density of vapour is wanted. And so the surface of the liquid is shifted in the apparatus while the ratio of the phases remains constant.

I may here mention that for this operation I constructed the compound hydraulic pump, which VAN ELDIK has used for his measurements on the capillarity of mixtures (Fig. III. Communication N^o 39 May '97). This apparatus seems to me preferable to the "analysateur" because the phases can be observed in a glass tube and need not come into contact with the packings but only with mercury and glass.

The influence of the packing on the observations with the "analysateur" has been mentioned previously. We have now to consider the influence of the operation mentioned on the result of the experiments.

The experiments, in so far as they deal with a temperature below the critical, will be considered sub. 5, it will here be sufficient to say that the experiments above the critical temperature have to decide whether the substance, originally in the liquid state (at an almost constant volume) will have a higher density when raised above the

critical temperature than the substance which originally was in gaseous state and assumes the same temperature and pressure. The movability of the pistons is of no consideration for the experiment above the critical temperature, the only important thing is that below the critical temperature the same distribution is obtained. DE HEEN had realized at the moment when the pistons are brought into their last position. One of the ways in which I obtained the distribution in an apparatus with two reservoirs of the ratio mentioned by DE HEEN in his second series was distillation.

Probably in choosing the ratio mentioned, DE HEEN expects to be able to separate from the gas above and from the liquid below a phase exclusively consisting of liquidogen or gasogen molecules than when the two reservoirs have the same volume. The substance chiefly consisting of gasogen molecules is related according to him to that consisting of liquidogen molecules as a dilute solution of salt in one more concentrated on which it floats. If the two have at some time been in contact the nearest approach to the original concentration of the two solutions of salt will be obtained by drawing off at one end the upper layers, at the other end the lower layers. In this reasoning we may put in the place of DE HEEN's hypothetical liquidogen molecules the really existing very small admixtures to the carbon dioxide. In the initially wholly or chiefly liquid portion of the carbon dioxide they amount to another admixture than in the initially wholly or chiefly gaseous portion and gradually they will be distributed equally by diffusion. According to § 2 it is obvious that greater corrections must be applied to the observed densities when the substance of which the density is measured is taken from the extreme layers than when they are taken from the intermediate layers. And so a more unequal distribution of the admixtures over the two reservoirs may also have attributed to the larger differences given by DE HEEN in his second series.

At any rate, now that DE HEEN's first series of which the results are systematically related to those of the second, has been refuted, his measurements of the second series do not in themselves prove his theses:

"Il est aisé de conclure de ce résultat que la densité critique n'a été admise jusqu'à présent est une densité purement fictive (further what has been cited in § 1). 3° la loi du diamètre est parfaitement observée, ainsi que la planche l'indique. Si l'on prolonge celui-ci jusqu'à la température critique, on obtient la densité critique *fictive* qui avait été admise jusqu'à présent, (4° Les courbes exprimant les variations de densité du liquide

de la vapeur se prolongent au dessus de la température critique, et ce n'est que vers 60° , en général que la masse devient homogène dans toutes les parties du tube (en employant toutefois les précautions indiquées)."

4. *Explanation of the deviations below the critical temperature.* DE HEEN's statement that for carbon dioxide in the case of the co-existence of liquid and vapour as far as about 20° below the critical temperature no definite densities would exist for the vapour and the liquid, but that for instance at 28° C. this density would be situated for vapour between the limiting values 0.288 and 0.533, for liquid 0.408 and 0.650, disagrees in my opinion with the experience of all who have made accurate measurements with liquefied gases.

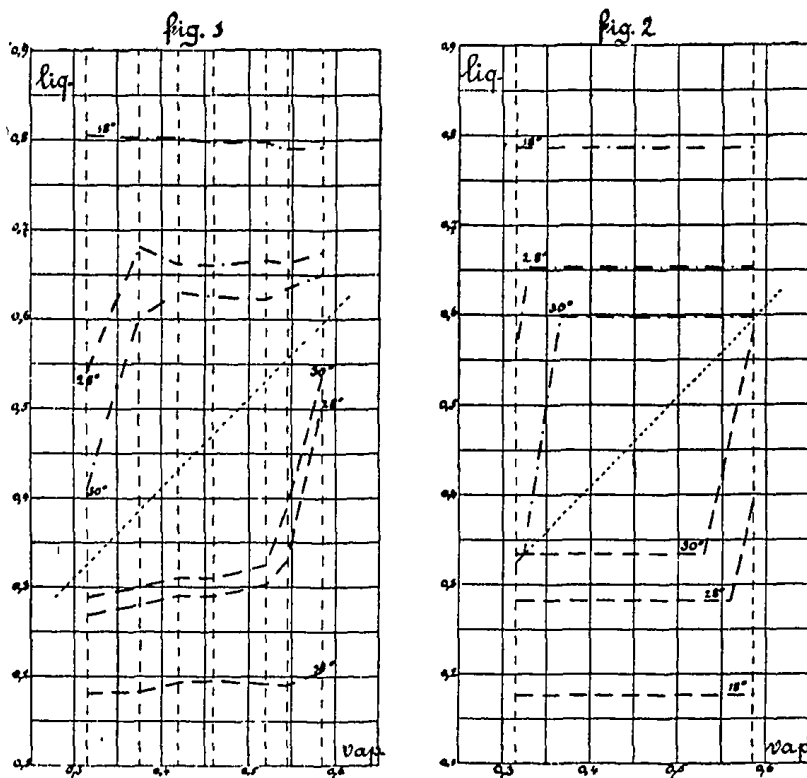
And though in repeating DE HEEN's determinations with the above-mentioned apparatus I have found small deviations from the liquid and vapour densities found by AMAGAT, they could always be attributed to errors of observation.

This statement of DE HEEN may be explained by the fact that the meniscus cannot be seen in the "analysateur." And so DE HEEN may have given as density of the vapour phase the mean density of matter in a reservoir in which the meniscus had risen already, and as density of the liquid phase the mean density of matter in a reservoir in which the liquid surface had fallen already.

Dr. VERSCHAFFELT has combined in a very clear diagram DE HEEN's data by plotting the densities given by the latter for the vapour phase and those given for the liquid as ordinates, and the mean density of matter in the two reservoirs of DE HEEN as abscissa. For simplicity I borrow from that diagram only a small number of lines (see fig. 1 p. 643) and give by its side in fig. 2 those which indicate the mean densities mentioned, in each of the reservoirs according to AMAGAT's vapour and liquid densities (the line applying at the critical temperature and higher, has been drawn at an angle of 45°).

It is obvious from these figures that DE HEEN in the calculation of his densities has neglected the correction from non-homogeneous to homogeneous substance. By applying this correction his observations would give a vapour and liquid density almost independent from the mean density of matter, which by means of corrections systematically related to those considered in §§ 2 and 3, would very likely be made to agree with those of AMAGAT within the limits of the errors of observation.

Everything being considered it appears desirable that DE HEEN should



repeat his experiments with due regard to the circumstances and the corrections indicated in this paper.

I think I have sufficiently justified the opinion that these experiments bring no arguments against the truth and the completeness of the theses from VAN DER WAALS' theory on the critical state mentioned at the beginning of § 1.

Physics. — Prof. VAN DER WAALS ON: "*The equation of state and the theory of cyclic motion*". III. (Continued from p. 584).

There is another quantity relating to the critical point, which calculated from the equation:

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT, \quad (1)$$

if b is kept constant, yields a value strongly deviating from what is found for it by means of the experiment. The quantity $\left(\frac{T}{p} \frac{dp}{dT}\right)$, calculated for the tension of saturated vapour, coincides in the critical