

Citation:

H. Kamerlingh Onnes & Perrier, A., Magnetic researches XIII. The susceptibility of liquid mixtures of oxygen and nitrogen and the influence of the mutual distance of the molecules upon paramagnetism, in:

KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 901-916

in the susceptibility to a fifth or sixth part of its value between the liquid state and the solid state at hydrogen temperatures. It now appears that a sudden change of this amount really exists, but takes place in two parts, namely, once to $\frac{1}{2}$ at freezing, and subsequently,

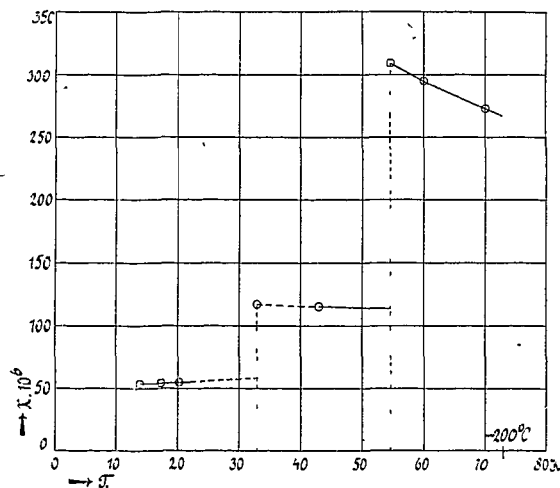


Fig. 2.

after the susceptibility has again increased a second time to $\frac{1}{2}$ at the transformation point -240° C., after which the susceptibility further decreases. In the accompanying figure our results are put together.

Physics. — “*Magnetic researches XIII. The susceptibility of liquid mixtures of oxygen and nitrogen, and the influence of the mutual distance of the molecules upon paramagnetism.*”

By ALBERT PERRIER and H. KAMERLINGH ONNES, Communication N°. 139d from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of January 31, 1914).

§ 1. *Introduction.* In 1910 and 1911 we published experiments upon the susceptibility of oxygen at very low temperatures, by which it was demonstrated that the specific susceptibility of this substance, which, in the gaseous form above 0° C. follows CURIE-LANGEVIN'S law, deviates considerably from this law in the liquid state at low temperatures, and even more so in the solid state.

Subsequently we have observed similar phenomena in other substances (paramagnetic salts). The (solid) substances referred to follow CURIE'S law at ordinary temperature, and also at temperatures that do not lie too far below it; but when the temperature falls to the

neighbourhood of the boiling point or the freezing point of hydrogen, they deviate from the law *in various degrees*¹⁾, but always in the direction of decrease of the susceptibility.

We think it advisable to recall here in a few words some of the views and hypotheses which guided us in the above-mentioned researches, in order to make clear the connection of the former experiments to each other, and to the determinations we shall here deal with, and to elucidate the object of these last.

When we began our magnetic investigations at low temperature (in 1908) we wished, amongst other things, to test LANGEVIN's recently published theory of paramagnetism which leads to CURIE's law, at low temperatures.

On this account (and on others, see Comm. N^o. 116, § 1) it was natural we should begin with oxygen. The deviations that we found in oxygen together with what we observed in other substances, gave us ground to suppose phenomenologically that there would be a law of corresponding conditions for the deviations from CURIE's law. This again gave rise to the question of how LANGEVIN's theory would have to be supplemented in view of the new phenomena. Our first idea was the possibility of polymerisation, which might take the form of association in oxygen. As the degree of association of liquid oxygen if diluted with a non-active substance, would be changed, and as diamagnetic nitrogen could serve as such a substance, we thought (see Comm. N^o. 116, § 5) that by experiments on mixtures with this substance we should be able to ascertain whether it was a case of polymerisation or not.

An experiment made with a less satisfactory apparatus than that which we now use, gave an indecisive result, and even led us to a wrong conclusion, as it seemed to support our assumption of the same change with temperature in the specific susceptibility of oxygen independent of the distance that separated the molecules from each other. In other words it still appeared possible to us that the specific susceptibility of oxygen vapour at the boiling-point might be the same as that of liquid oxygen, and that therefore gaseous oxygen at this temperature would deviate from CURIE's law to the same extent as liquid oxygen. Our intention soon to make further measurements on mixtures of oxygen and nitrogen, came to nothing, as one of us left Leiden. It was a considerable time before we were able to continue our experiments.

In the mean time, KAMERLINGH ONNES and OOSTERHUIS's investiga-

¹⁾ KAMERLINGH ONNES and PERRIER, Comm. Nos. 116, 122a, 124a.

tions again raised the idea that the distance of the molecules in a paramagnetic substance certainly has an influence upon the deviations from CURIE'S law. Their investigation of oxygen of more than 100 times the normal density (Comm. N^o. 134*d* April 1913) demonstrated more specially that the susceptibility for gaseous oxygen can be represented down to -130° C. with CURIE'S constant, which holds for the ordinary temperature, which indicated the possibility that this might still be the case at -183° C. This gave fresh support to what they added at the end of their paper of Jan. 1913 (Comm. N^o. 132*e*), showing the desirability of experiments upon the question, whether the bringing of the molecules (or atoms) of a paramagnetic substance to a greater distance from each other, influences in itself the deviations from CURIE'S law, and pointing out the importance of the continuation of our experiments with liquid mixtures of oxygen and nitrogen.¹⁾

Before we could at last begin these experiments in 1913 the importance of them was increased by yet another circumstance. Besides the hypotheses considered in the above mentioned article, hypotheses of another kind arose²⁾.

With the former hypotheses, we do not interfere with the law of equipartition, but assume either polymerisation, as in the above case, or a subsidiary potential energy, a "molecular" field, the magnitude of which is determined, not only by the field, but also by the amount of one-sidedness of the direction of the molecular magnetic axes (WEISS and FOËX, KAMERLINGH ONNES and OOSTERHUIS)³⁾. In the new type (OOSTERHUIS, KEESOM) on the other hand a distribution of energy

¹⁾ Recently, WEISS (C. R. Dec. 1913) in deducing the distance law for the molecular field in ferromagnetic substances (comp. § 4 this Comm) points out the importance of investigations of the same material at different densities. See also G. FOËX, Arch. d. Sc. phys. et natur. Genève (4) XXXV. 1913.

²⁾ As had been partly the case with the hypotheses of the first kind, so also those of the new kind were partly suggested by our former magnetic investigations.

³⁾ The hypothesis, that the resultant magnetic moment of the molecule changes, can be introduced in two different ways. In the first place, by assuming polymerisation, as mentioned above. In the second place by supposing that the change takes place exclusively within the molecule itself. By continuous change of this sort of course every deviation from CURIE'S law may be explained. In that case there can be no question of decision between the above mentioned types of theory. The supposition referred to seems less acceptable also for this reason that in the cases in which WEISS was led to assume a change in the molecular moment, this was always a discontinuous alteration (by changes in the number of magnetons) and one which took place in all the molecules at once, while for the rest the moment within a definite temperature zone did not undergo any change.

is supposed, which is determined according to the quantum-theory.

In the extreme form of this type no other suppositions are introduced than those of the quantum-theory. There is naturally room for transitional forms between this extreme form and the other type of hypothesis. These are got by assuming polymerisations or a molecular field besides the quantum-theory.

It is now of importance, not only for magnetism, but also for the law of molecular activity in general, to decide between these two different types of hypothesis, by experiment. The most important for this purpose are experiments in which the paramagnetic molecules are brought to different distances from each other. For if the above mentioned question should be answered in the negative and it should be proved that the susceptibility per molecule remained the same at whatever distance they are from each other, then all hypotheses of the first sort (mutual influences) would of course fall to the ground. The measurements which should demonstrate this would be an *experimentum crucis*.

The determination of the susceptibility of liquid mixtures of oxygen and nitrogen claims the first place in experiments upon the influence of the distance of the molecules upon the deviations from CURIE'S law. The liquid (paramagnetic) oxygen exercises no chemical influence whatever upon the liquid (diamagnetic) nitrogen; the two substances can be mixed in any proportions, so that the distance of the paramagnetic oxygen molecules can be increased at pleasure: the mixtures remain moreover liquid down to a very low temperature, which is of particular importance, if the theory of quanta is to be applied. Experiments with these mixtures promised therefore a more distinct and more immediate decision than those with crystals and solutions of chemical compounds in different degrees of dilution¹⁾. In the investigation now completed we have not been able to do more than make a first survey of the difficult territory.

We here offer our sincere thanks to Dr. OOSTERHUIS, who has contributed greatly to the success of our work, by very carefully measuring out the field that served for our experiments, and by repeating certain susceptibility determinations which were doubtful. His measurements enabled us to introduce important corrections in our results.

¹⁾ With regard to these we may remark that the important investigations by CABRERA and MOLES (Arch. d. Genève (4) XXXV, May 1913) of solutions of iron salts are of a chemical nature and assume the validity of CURIE'S law. Their object is therefore quite different from ours, in which the point is to investigate the influence of the distance of the molecules of a *chemical element* dissolved in another *element*, upon a function of the temperature.

§ 2. *Method.* The measurements were made by the attraction method, with a vertical cylinder of the substance to be investigated. One of the extremities of the cylinder is placed in the middle of the interferrum of an electromagnet. As in the apparatus previously constructed by us ¹⁾ the cylinder was attached to a vertically running carrier, and the forces were measured by a zero-method; in this the modification introduced by OOSTERHUIS ²⁾ was made use of, viz. the current through the electro-magnet was regulated, and therefore the field adjusted, until there was equilibrium with marked weights.

While thus the magnetic part of the experiments is about the same as that of the previous ones, the arrangement of the actual experimental object demands a number of special apparatus and precautions. A homogeneous mixture must be prepared of known proportion, and in a proportion chosen at will, of two substances, which are gaseous at ordinary temperature, and which are condensed in the experimental tube.

In the first place a communication must be made through the closed outer cover of the cryomagnetic apparatus (see description loc. cit.) with the apparatus for mixing and measuring the gases. For this purpose, the glass tube *A* (see fig. 1), which forms the central part of the carrier, is bent round three times rectangularly at *B*; further it bears a horizontal tap *C*, and terminates in a horizontal ground joint *D*, in which fits the ground extremity of the tube *E*, which protrudes outside. This tube is enclosed in a thick but elastic india-rubber covering, and can be pulled back about 2 centimetres, from outside, and made fast in this new position; in this way the connection with the carrier can be made: or the latter can be left *quite free*, without the cover being opened. In the same way the tap *C* can be manipulated from the outside by means of a similar arrangement *F*.

The necessity of the mixture being homogeneous, entails vigorous stirring inside the experimental tube (the cylinder *R*, at the lower end of the carrier). Even when the mixture is homogeneous in the gaseous form, the oxygen which condenses more easily, will tend to collect at the bottom in the carrier; this difficulty is overcome by using a stirrer consisting of a very long thin glass capillary tube *G*, terminating in a small disk *H* (the actual stirrer), which carries a little piece of iron (*K*) at the top, the whole of which can be moved up and down through a distance equal to the height of the experimental tube. This movement is set in motion by the attraction

¹⁾ See H. KAMERLINGH ONNES and ALB. PERRIER, Comm. No. 139a.

²⁾ E. OOSTERHUIS, Comm. No. 139b.

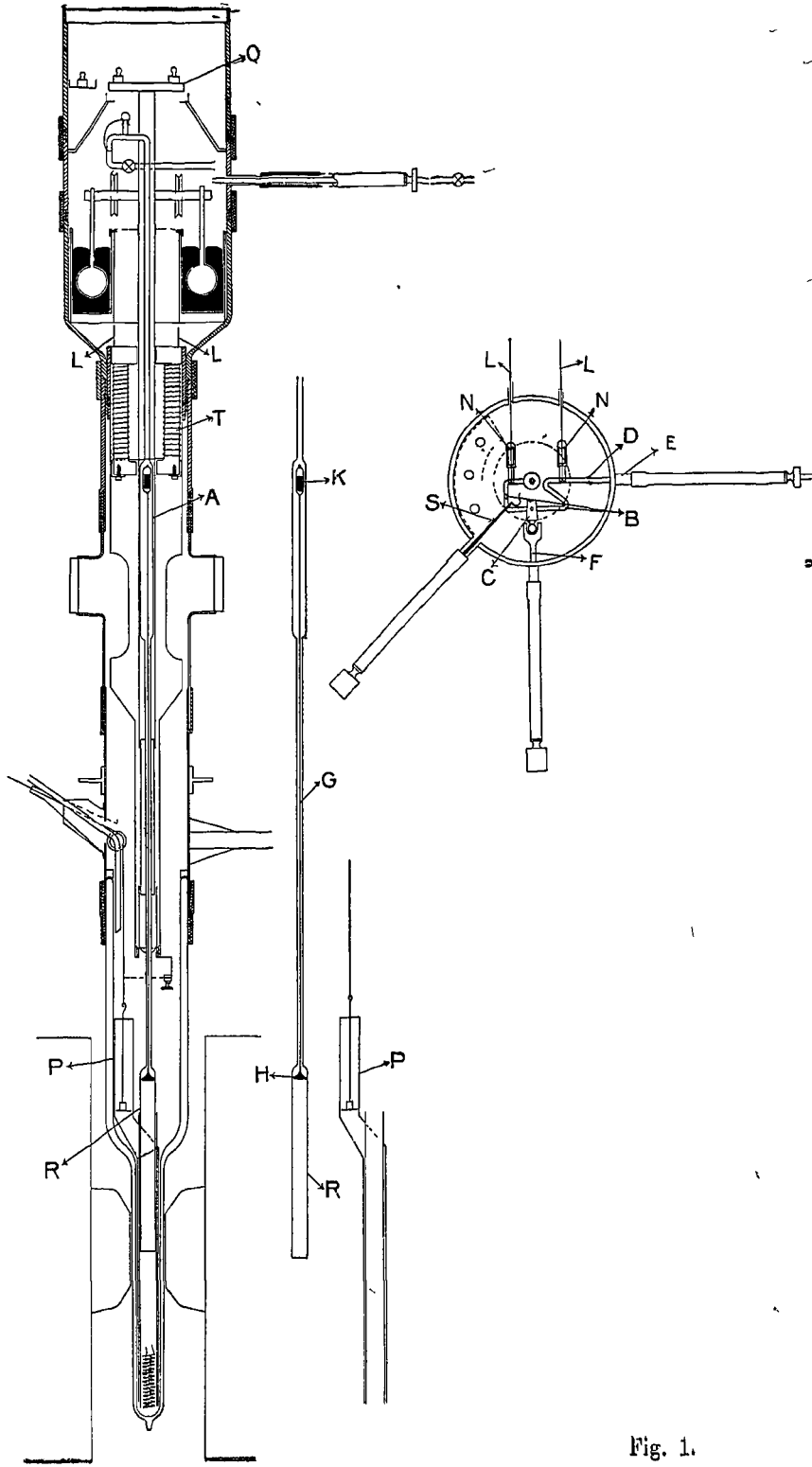


Fig. 1.

of an electromagnet I upon the piece of iron K ; the electro-magnet is moved from outside the apparatus by means of two bronze strips L , which run over the pulleys N and pass through the walls without friction, terminating in two elastic enclosures similar to F and E . These suspension-strips, which also serve as conductors for the electro-magnet, are moved by hand.

The carrier is provided at B with a small stopper serving as a safety valve, to guard against a casual excess of pressure in the carrier during the measurements, when the tap is closed, bursting the carrier.

The preparations for a series of measurements took place in the following order: when the enclosure is found to be air-tight, a sufficient weight is placed upon the plate Q to bring the carrier to its lowest position; the connection with the tube E can then be made, the tap C is then opened, and any gases that may be contained in the carrier, are pumped out. Then the cryogen bath (of pure liquid nitrogen) is made ready, and the temperature reduced to a few degrees below the boiling-point by reduction of the pressure. Finally the desired amount of pure oxygen, which has been previously measured in a volumometer resembling a TÖPLER-pump, can be condensed in the carrier, and then by means of the same instrument, the quantity of pure nitrogen required to completely fill the experimental tube R . After this C is shut, D is disconnected, the gas supply tube is pulled back and the overweight taken away; the carrier is then free, and completely closed against the vapour of the bath. While the bath is being brought to atmospheric pressure, and to an even temperature, which is greatly promoted by the pump-stirrer P^1), which causes a vertical circulation in the whole bath, the electro-magnet, which serves as stirrer for the mixture, is put in motion, until the magnetic attraction, which is measured from time to time, reaches a constant value.

The question of what the composition of the mixture is deserves particular attention. A *given weight* of oxygen is introduced into the tube, which spreads over a given volume, known by the calibration of the experimental tube. The weight of oxygen per cm^3 , i. e. the concentration, is thus given by immediate experiment, which quantity is also the most important from the magnetic point of view, as the measurements in the first place give the susceptibility of the mixture, and the concentration enables us to deduce from it the specific magnetism which can be ascribed to the oxygen

¹⁾ See H. KAMERLINGH ONNES, Comm. No. 123, § 2.

alone. To compensate the vacuum caused by the contraction of the mixture by each decrease of temperature, we have each time added *pure nitrogen* (stirring of course each time); our object was the investigation of the influence of the mean *distance* of the paramagnetic molecules upon the magnetisation, and the process described above apparently comes to the determination of the changes in the magnetisation with the temperature, for every mixture at *constant distance* of the oxygen molecules.

After the measurements the vapour products were collected, and analysed with pyrogallic acid. This analysis is a useful check, but cannot lay claim to great accuracy, as the comparison with the synthesis assumes the knowledge of the total quantity of condensed nitrogen (including the amount added during the measurements), which quantity is for various reasons somewhat uncertain. Moreover it is necessary that the vapour products should be very completely collected, as a considerable weight attaches to what is vaporised last, as being almost pure oxygen. On the other hand we may remark that the deduction of the concentration (see above) from the synthesis presumes only an accurate knowledge of the *weight of oxygen* and not that of the nitrogen, and therefore can claim a greater degree of accuracy.

The susceptibilities are expressed in absolute units by comparison with that of pure liquid oxygen, which are previously measured in absolute value by the method of rise ¹⁾; this calibration comes simply to this, that a series of measurements are made under the same conditions as the former, but with pure oxygen instead of with the mixtures. Moreover, a calculation of the absolute values based upon the values of the field according to the measurements made by Dr. OOSTERHUIS in Leiden after the measurements, lead to results which agreed with the experiments previously obtained, well within the limits of experimental accuracy. Further the magnetic corrections were applied for the glass of the carrier and for the nitrogen of the bath as well as of the mixture ²⁾.

§ 3. *Conclusions and experimental results.* The mean numerical data of the measurements are given in table I, where χ signifies the magnetisation of 1 gram of oxygen in each of the mixtures or in the pure oxygen; for the latter the values are calculated on the

¹⁾ KAMERLINGH ONNES and PERRIER, Comm. No. 116. Cf. note 1, p. 912

²⁾ These corrections must be made even in a purely relative measurement, as they are by no means proportional to the susceptibility of the experimental object taken as a whole.

basis of our measurements in 1910 (Comm. N°. 116); ρ is in each case the weight of oxygen per cm³. (concentration), λ the approximate ratio between this weight and the corresponding one in the pure liquid; λ indicates to some extent the dilution (only approximately, because with the method followed λ changes with the temperature)¹⁾.

TABLE I.

Magnetisation-coefficients for oxygen. (77. ^o 4 K—64. ^o 2 K)									
	ρ		$(p = \text{atm. pressure})$		$(p = 300 \text{ mm.})$		$(p = 100 \text{ mm.})$		
			t	$\chi \cdot 10^6$	t	$\chi \cdot 10^6$	t	$\chi \cdot 10^6$	
liquid oxygen pure	1.204		-195 ^o .65	259.6	-202 ^o .2 ₃	271.4	-208 ^o .8 ₄	284.9	
	1.235								
	1.267								
Mixtures	I	0.745 ₈	$\frac{3}{5}$	-195 ^o .65	294.5	-202 ^o .2 ₃	314.5	-208.8 ₄	336.5
	II	0.401 ₀	$\frac{1}{3}$.79	336.7	"	359.6	"	390.6
	III ₁	0.230 ₄	$\frac{2}{11}$.60	363.8	"	393.0	"	[423.5]
	IV	0.138 ₀	$\frac{1}{9}$.65	383.6	-202 ^o .2 ₃	420.4	"	459.8
	V	0.080 ₁	$\frac{1}{15}$	-195 ^o .80	395.8	—	—	-208.8 ₄	472.0
extrapolated by $\chi = \frac{0.03097}{T}$ (WEISS and PICCARD at 20 ^o C.)				-195 ^o .65	400.0	-202 ^o .2 ₃	437.2	-208 ^o .8 ₄	482.2

Table I shows at once this qualitative result: *The specific magnetisation coefficient of oxygen becomes considerably greater, in pro-*

¹⁾ The various numerical data upon which the results are based are not all of the same degree of accuracy: the temperatures, measured by means of the pressure under which the liquid boils, the same pressures being chosen for the different mixtures, may be compared in the one and the other mixture to 0.1^o, the absolute values, on the other hand, have the same degree of accuracy as the vapour pressure curves.

The directly found (volume) susceptibilities of the mixtures, which are not included in the table, may be compared with one another to about 0.3% on an average. As regards the *specific magnetisation coefficients*, if these may be compared for the same mixture at different temperatures with the same accuracy as the susceptibility, their uncertainty in *absolute value* is specially determined by that of the concentration; we estimate it on an average at 1.5%, higher for the large concentrations, lower for the smaller ones.

portion as the concentration diminishes, i. e. the additive rule is by no means followed in mixtures of oxygen and nitrogen. From a somewhat more careful inspection, and the comparison with the last row of the table, it appears further that with increasing dilution the magnetisation coefficient approaches to the values which satisfy the inverse proportionality with the absolute temperature, starting from the number lately obtained by WEISS and PICCARD for gaseous oxygen (see also Fig. 3).

Without anticipating in any way the theoretical interpretation of these results, which will be treated in the next paragraph, we can phenomenologically express them as follows:

The deviations from CURIE-LANGEVIN's law, shown by pure oxygen at low temperature, are not an immediate consequence of the change of temperature, but are caused by the increase of the density or by the distance between the molecules becoming smaller.

Finally, let us examine more closely the thermal change for each concentration, by plotting $1/\chi$ as a function of T (Fig. 2). We see at once that the points obtained lie upon parallel straight lines; the

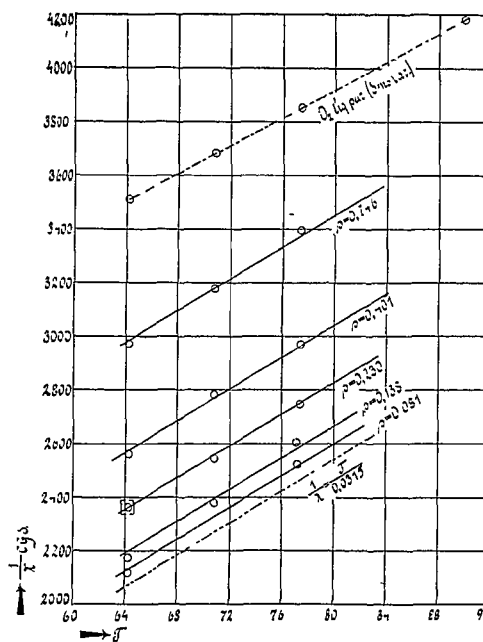


Fig. 2.

change with the temperature can therefore be represented ¹⁾ within the limits of accuracy of the observations, by a relation of the form

¹⁾ As was found by KAMERLINGH ONNES and OOSTERHUIS for liquid oxygen; Comm. N^o. 132e.

$$\chi(T+\Delta) = \text{const.},$$

in which only the parameter Δ changes from one concentration to the other. Table II shows this:

TABLE II.

Mixture	Δ	$\chi(T+\Delta)$		
		$T = 77.4_4$	$T = 70.8_6$	$T = 64.2_5$
I	29.5	0.0315 ₇	0.0316	0.0315
II	16.3	316	313	315
III	9.5	316	316	[312 ₅]
IV	4.5	314	316	316
V	2.2	316	—	314
Mean 0.0315 ₂				

Therefore: the change in density of the oxygen only alters the specific magnetisation, without changing the CURIE-constant.

The pure liquid oxygen seems to form an exception: the straight line $1/\chi = f(T)$ for this differs considerably in direction from that for the mixtures. We would call attention to the fact, however, that each mixture was examined at constant concentration (see § 2); while this was not the case with pure oxygen, which shrinks considerably on cooling (10% about between -183° and -210°); if we calculate for any temperature (say -195°) the specific magnetisation that pure oxygen would have at that temperature and at the densities corresponding to the other temperatures, using the CURIE-constant which is common to the mixtures at constant concentration, the values obtained thus (see Fig. 3 the points indicated by black disks) fall in a natural way upon the general curve, which gives the specific magnetisation as a function of the concentration at the temperature under consideration; the data obtained from these measurements form therefore strong arguments in favour of the conclusion that in the investigation of pure liquid oxygen at constant density a curve for the change of the magnetisation would appear, which only differed from that for the mixtures by a new translation. This causes the anomaly to disappear. The strict experimental proof of this conclusion can only be obtained by a great number of experiments with a very concentrated liquid, or by means of a direct experiment, in which we begin

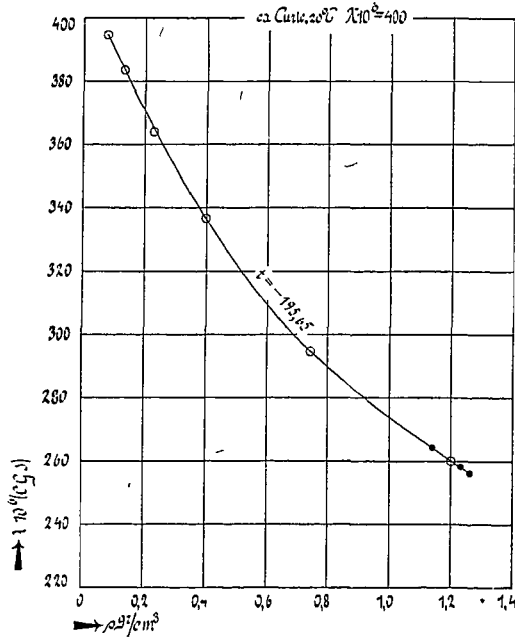


Fig. 3.

with pure oxygen and for each decrease of temperature add the necessary quantity of nitrogen ¹⁾).

§ 4. *Theoretical conclusions.* We must call attention to the fact that every theoretical interpretation of our results must account for two different facts: in the first place for the change of the magnetisation with the density, and in the second place the parallelism of the lines $\frac{1}{\chi} = f(T)$.

It is plain that *LANGÉVIN's theory, only supplemented by the hypothesis of the negative molecular fields, is sufficient to give the explanation.* In fact if N represents the coefficient of the molecular field, it leads to the law

$$\frac{1}{\chi} = \frac{T}{C} + Nq \dots \dots \dots (1)$$

or

$$\chi(T + \Delta) = C, \text{ where } \Delta = CNq,$$

¹⁾ Experiments make it probable, that for gaseous oxygen χ even at -183°U. does not deviate or at least (see the conclusion of § 4) deviates only very little from *CURIE's law.* In the application of the ascension method χ may therefore not be supposed to be equal for the liquid and for the vapour, as was done in formula (2) of Comm. No. 116, but a correction must be applied, which, however, in our case remains within the limits of experimental error.

which agrees with the law following from Table II, if we assume that Δ or $N\varrho$ decreases with the density.

This being established, the experiments further permit, and this gives them an additional significance, to account for the way in which the molecular field changes with the density or with the distance of the molecules.

We remark in the first place, that the accurate calculation of the molecular fields rests upon the knowledge of the deviations from CURIE'S law, and not upon that of the susceptibilities themselves [formula (1)]. It would therefore be necessary to know the specific magnetisations in absolute value down to at least 0.1% in order to be able to deduce the fields from them with sufficient certainty, this is especially the case for the great dilutions where the deviations are extremely small. A determination of this degree of accuracy demands in itself a long and difficult special investigation with perfected apparatus.

The solution, if not completely found, may yet be brought within narrow limits. The first question that then arises is, whether the field is equal to a particular power of the distance of the molecules i. e. of the density. If we suppose $N = a\varrho^n$, then the molecular field is $a\varrho^{n+1}$. At constant temperature $1/\chi = f(\varrho)$ is then a parabola of the degree $n + 1$, with the axis vertical and the top on the axis of ordinates. For $n = 0$, $1/\chi$ is represented by a straight line.

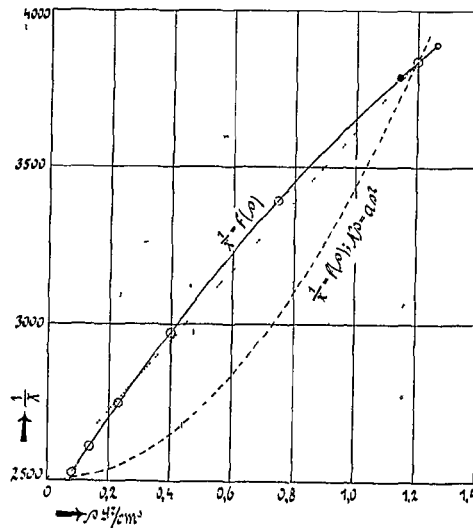


Fig. 4.

In Fig. 4, the curve which our experimental data give for the temperature 77°.45 K. is shown; it deviates from the straight line,

but the deviations are not much greater than the errors of observation, except for the most diluted mixture. Moreover the slight curvature is *in the opposite sense to all the parabolae for which $n > 0$* . The observations at concentrations smaller than 0.1 indicate that the molecular field then begins to change more quickly, but they do not justify the assertion that this is actually the case. It is therefore not probable that the results can be represented by means of a positive n (except for very great dilutions, for which we have not a single indication); in order to elucidate this point we have also constructed the curve $1/\zeta = f(\varrho)$, which with the same extremities corresponds to $n = 1$, i. e. to the law that the molecular field would be proportional to the square of the density or to the inverse sixth power of the mean distance of the molecules; it is obvious that this bears no resemblance to the experimental curve.

We assume therefore *that the molecular field of oxygen changes about proportionally to the density*¹⁾.

This law, in the case of the appearance of a negative field (assuming that this exists) for oxygen, differs totally from that at which WEISS arrived, in the case of the positive molecular field with alloys of ferromagnetic metals, for the dependence of N upon the density, and from which he inferred an influence according to the inverse sixth power of the distance, which for that reason we have just referred to. (From our law, in the same way, an influence according to the inverse third power of the distance would follow).

At present, we need not see any contradiction between these two results, as the conditions for which the two laws of distance hold good, are quite different. This applies both to the nature of the substances and to the state of aggregation in which they were examined. Moreover it must be particularly borne in mind that the sign for the molecular field is different in both cases. The part of the curves referring to the change of N with the concentration, which WEISS makes use of in his theory, lies entirely in positive fields, the transition to negative fields is curved. We are in complete ignorance as to the origin of the mysterious influences which cause the phenomena ascribed to the molecular field. There is no ground therefore to expect that the two fields are subject to the same law. Should it be confirmed that the two kinds of molecular field depend upon the distance of the molecules according to different laws, we

¹⁾ Cf. the next paper by KAMERLINGH ONNES and OOSTERHUIS, in which the idea of the dependence of Δ on the concentration is extended to the "atomic concentration" of the paramagnetic component in crystallized compounds, in the first place in those containing water of crystallization.

might even see in this a proof that in the two cases influences are at work which are the effect of different causes¹⁾.

If we continue the idea that the deviations from CURIE'S law are to be attributed to a negative field, we come with the value 0,03152 which we deduce for CURIE'S constant, to 14.11 magnetons per molecule of 2 rigidly connected atoms, while WEISS and PICCARD, from their determination of the constant for gaseous oxygen arrive at exactly 14. An error of 0.2 degrees in the lowest temperature at which we made observations would explain this difference. So there is no reason to take this observation as at variance with the law of magnetons. [At the end of § 4 we have drawn attention to a circumstance that would possibly explain the difference. (Added in the translation)].

Although the hypothesis of the negative molecular field is sufficient to describe the phenomena, it is not devoid of interest to consider in how far the other hypotheses can be reconciled to the observations.

As regards the polymerisation-hypothesis, it is not probable that the association decreases as rapidly with the density at constant temperature as would have to be the case if the experiments were to be explained by it, nor that the result of a given form of the hypothesis, which might give this change, would lead to the set of parallel straight lines in fig. 2.

OOSTERHUIS'S hypothesis, that the energy of rotation should take the form of

$$U_r = \frac{h\nu}{e^{kT}-1} + \frac{h\nu}{2}$$

must be supplemented by a further hypothesis. It is in the line of the deduction to accept that the moment of inertia of the molecule changes considerably by dilution, and increases to very great values. Even in accepting this hypothesis it appears from calculations by DR. OOSTERHUIS that the deviations of the curves calculated from the set of the parallel straight lines in fig. 2 are too large to be explained by experimental errors²⁾.

¹⁾ The function $\rho^{4/3}$, which was given in a preliminary note (Soc. Suisse de physique, Frauenfeld 1913) was based upon data which later appeared to have been insufficient in number, and before some subsequently calculated corrections had been applied. The function may be correct for a range of weak concentrations.

²⁾ In these calculations OOSTERHUIS started from the values of Δ which were deduced immediately from the experiments according to Table II, which in particular gives the most probable slope of the straight lines accepted to be parallel.

Finally we may remark that the supposition

$$\chi = f(T) + N\phi \dots \dots \dots (3)$$

combines the various hypotheses which we have explained above (except that of polymerisation), and agrees with our experiments if $f(T)$ is independent of the density, and N of the temperature ¹⁾. It accounts for all phenomena which are expressed by a parallel displacement whatever value is ascribed to $f(T)$, if only it remains independent of the density.

[One can imagine that $f(T)$ is in reality of such a form that in the temperature-range of our experiments it gives for χ of the oxygen in the liquid mixtures of oxygen and nitrogen a value which, while being small for the large densities of oxygen, increases in passing to more and more high dilutions, and approaches in the limit to a value *greater* than that which with CURIE's law is obtained from WEISS and PICCARD's experiments. If further experiments which may be undertaken with a view to throwing light upon this point should give a positive result, one could explain without relying upon experimental error the slope of our lines for χ being a little small (given by $C = 0,0315$, see fig. 2). It would then be of interest to compare that result with what the investigation by KAMERLINGH ONNES and OOSTERHUIS on the susceptibility of gaseous oxygen at low temperatures will teach when extended to lower temperatures. It is not entirely excluded that the nitrogen plays a different part from a vacuum. Added in the translation.] (Cf. note 1 p. 915. Added in going to press).

Since then Dr KEESOM has communicated to us that by calculating the values of Δ in giving to $f(T)$ [see formula (3)] either OOSTERHUIS's form, or the form which KEESOM has developed in Suppl. N^o. 32a, whereby the values of χ are a little changed, one obtains a satisfactory representation. The values of Δ are then in agreement with the function χ^2/ρ for large values of ρ , which he arrives at (see a paper of his to be published shortly). In his calculations KEESOM accepted the number of magnetons of WEISS and PICCARD. His theory explains also that the curve $\chi = f(\rho)$ of fig 4 does not pass through the origin. [Note added in going to press.]

¹⁾ $f(T)$ represents the energy of rotation as a function of the temperature. (3) is only applicable to the range where the magnetisation is strictly parallel to the field. Formula (3) includes inter alia the vanishing of the CURIE point in ferromagnetic substances caused by zero energy deduced by KEESOM (Leid. Com. Suppl. N^o. 32a and b (1913)).

[Regarding the influence of the density on $f(T)$ in KEESOM's theory see his next paper, cf. also note 2 p. 6 of Suppl. N^o. 32a. Added in going to press.]