had resulted in an appreciable increase of the purity of the gas. The
log p, T—¹-curve (*p* in mm Hg.) now showed no abnormal variation of the
slope, *vide* Fig. 3, where the dashed line (- - - -) refers to measurements on
the sample purified by fractional evaporation, the full line (——) to those
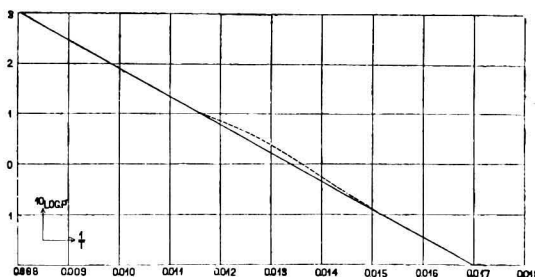

Fig. 3.

on the sample purified by rectification. Numerical data concerning the
vapour pressures of krypton will be given in a subsequent paper.

To check the purity of the gas now obtained the middle and the last
fractions mentioned above were added together [1]) and rectified again in an
apparatus as described under *a*, but of smaller dimensions. In this apparatus
the double-speeded screw was 4 cm long, diameter 8 mm, depth of the
thread 1,5 mm. The vapour pressures of the middle fraction obtained by
this new rectification coincided with those of the product of the first
rectification. We conclude that rectification is a much more effective
method of purification than fractional evaporation.

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[1]) Rectifying the middle portion alone was prohibited by its small quantity.

Physics. — *On the adsorption of neon on glass at liquid hydrogen temperatures.* By W. H. KEESOM and G. SCHMIDT. (Communication N⁰. 226a from the KAMERLINGH ONNES Laboratory at Leiden.)

(Communicated at the meeting of September 30, 1933).

Summary. Measurements have been made on the adsorption of neon on glass at four
temperatures in the liquid hydrogen range. It appeared that in increasing the pressure the
covering of the wall proceeds regularly and that complete covering with a monomolecular
layer is reached at about the saturated vapour pressure. The adsorption isotherms are
represented pretty well by the formula :

$$q^3 = \frac{p}{0.7\,(p_s - p) + p},$$

q being the fraction of the wall covered, *p* the pressure, p_s the saturated vapour pressure.

§ 1. *Introduction.* When trying to measure temperatures below 1°K.
by means of a helium thermometer with an ice point pressure of 1 mm
mercury, it appeared that already below 4°K. the pressure decreased too
rapidly, and that at 0.73°K. (derived from the vapour pressure of the liquid

helium) the pressure in the thermometer had nearly vanished. We realised that a complete monomolecular covering of the inner wall was just sufficient to take up nearly all the helium present.

This experience induced us to make an examination of the adsorption of helium on glass at liquid helium temperatures. We decided, however, to start with an investigation of the adsorption of neon at liquid hydrogen temperatures.

For the different theories of adsorption we refer to LANGMUIR[1], MAGNUS and others[2].

Measurements have been made on argon, nitrogen, oxygen and carbon monoxide, on glass and on mica, already by LANGMUIR. The experimental material is, however, not yet sufficient to get a good survey of the course of the adsorption isotherm over the whole range.

Of the noble gases, of which one can feel sure that adsorption has a purely physical character, only argon has been investigated with respect to glass and mica[1]. The measurements are, however, incomplete.

Measurements of the adsorption of neon, helium, and hydrogen by a perfectly smooth surface, such as a glass wall, are completely lacking. Only some measurements on adsorption by charcoal have been made.

It is in the first place interesting to examine for these gases how the covering of a glass wall with adsorbed gas proceeds if an adsorption isotherm is followed till saturation sets in. This paper deals with such an examination for neon. In a following paper some results about helium will be communicated.

§ 2. *The apparatus.* Our method consisted in comparing the pressures of two gasthermometers (Fig. 1), identical as to the volumes of the different parts, but different as to the glass surface. For this purpose the thermometer T_1 had been filled with a large number of thinwalled glass capillaries of which the total surface and the glass volume were known. The remaining volume was as nearly as possible equal to that of T_2.
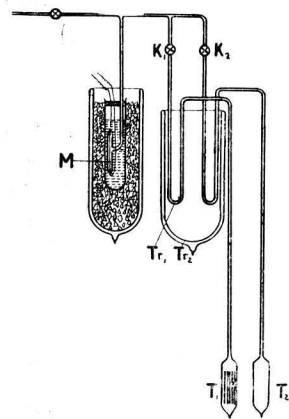
The thermometer spaces could be connected by the cocks K_1 and K_2 respectively with a common manometer space, the pressure of which could be measured with a hot wire manometer M immersed in an ice bath. The volume of this manometer space could be considered as a relatively small dead space.

The two capillaries were identically bent to small moisture traps Tr_1, Tr_2 cooled with liquid air. The thermometers and the capillaries were taken from the same tube of Thüringen glass.

Fig. 1.

[1] I. LANGMUIR, Journ. Amer. Chem. Soc. **40**, 1361, 1918.
[2] Trans. Far. Soc. **28**, 131—394, 1932.

Gas volume in the thermometerbulb: 5.426 cm³ (20° C), inner diameter thermometer capillary: 2.05 mm, inner glass surface of T_1: 266 cm².

§ 3. *The measurements.* For outgassing the cocks, the thermometer and manometer spaces were kept at high vacuum during several days before a series of measurements was to be made. The remaining gas development could be controlled with the hot wire manometer.

The last day before the measurements both thermometer bulbs together with large parts of the capillaries were heated to 340°C. for several hours. During this operation the moisture traps were surrounded by liquid air; they remained so till on the next day the measurements had been finished. On this day the hot wire manometer was compared with an accurately calibrated Mc LEOD gauge.

A series of measurements proceeded as follows. When both thermometers had been highly evacuated, the cocks K_1 and K_2 were closed. Then the manometer space was filled by connecting it with a neon container of about 3 1 capacity held at constant temperature. Alternately such a filling was introduced into each of the thermometer bulbs.

If there had been no adsorption, the pressures of the two thermometers would have increased with equal amounts. The adsorption manifested itself by the difference in increase of the pressure of the two thermometers.

In this way we could rather rapidly take a complete series of points of an adsorption isotherm.

The manometer volume was so small compared with the thermometer volume, that practically at each step the same quantity of gas was introduced into the thermometer. When necessary a small correction was applied.

This made it possible to determine in a simple way the thermomolecular pressure difference. For determining the pressure obtained in thermometer T_2 after a large number of fillings, we consider the thermomolecular pressure difference, which in this case is small, as being sufficiently well known. Neglecting the adsorption in T_2 we can then calculate the pressures in T_2 after the different fillings. By comparison with the values given by the hot wire manometer we get the thermomolecular pressure difference as a function of pressure. After having calculated the adsorption in T_2 a correction for the small adsorption in T_2 can be applied.

In our case this determination of the thermomolecular pressure difference served rather as a control because we could already dispose of an extended experimental material *i.a.* for neon (to be published before long).

After the measurements the hot wire manometer was again compared with the Mc LEOD gauge.

We checked the purity of our neon by filling thermometer T_2 with neon to saturation and seeing whether the pressure increased if more neon was introduced. The small pressure increase which occurred (at constant tem-

perature) pointed to a small admixture of helium which, however, is of no importance for our results.

§ 4a. *The results* have been collected in table I. It gives the equilibrium gas density as a function of the fraction of the wall that is

TABLE I.

Adsorbtion of neon on glass							
$T = 20.28$ °K. $p_s = 35.6$ mm Hg		$T = 16.99$ °K. $p_s = 3.93$ mm Hg		$T = 15.86$ °K. $p_s = 1.51$ mm Hg		$T = 14.45$ °K. $p_s = 0.294$ mm Hg	
p (mm Hg)	q	p (mm Hg)	q	p (mm Hg)	q	p (mm Hg)	q
0.0471	0.106	0.0149	0.223	0.0017	0.138	0.0015	0.133
0.103	0.140	0.0525	0.312	0.0085	0.292	0.0051	0.296
0.163	0.179	0.0967	0 356	0.0255	0.389	0.0146	0.417
0.227	0.196	0.445	0.540	0.0482	0.438	0.0311	0.500
0.289	0.212	0.818	0.621	0.118	0.549	0.0524	0.556
0.347	0.232	1.192	0.680	0.193	0.620	0.0760	0.587
0.407	0.251	1.557	0.749	0.279	0.690	0.0952	0.660
0.469	0.260	1.931	0.790	0.404	0.741	0.120	0.700
0.530	0.265	2.294	0.855	0.522	0.807	0.144	0.753
0.601	0.275	2.656	0.913	0.648	0 828	0.166	0.789
0.763	0.312			0.763	0.862	0.187	0.823
				0.882	0.904	0.221	0.858
				0 997	0.943	0.237	0.892
				1.116	0.967	0.259	0.922
				1.232	0.978	0.282	0.945
				1.340	0.990		
				1.446	1.001		

covered with adsorbed gas. Instead of the gas density itself, the gas pressure p is given which corresponds with this density at 20.28°K. (obtained by multiplying the real pressure by $20.28/T$) [1]. p_s is in the same scale, *i.e.* measured as a pressure at 20.28°K., the saturated vapour density. The number q, which indicates the fraction of the wall covered, is obtained by dividing the quantity of gas adsorbed by the quantity which would correspond to a monomolecular layer covering the wall. This monomolecular

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[1] Deviations from the ideal gas laws may be neglected here.

layer is supposed to consist of spheres arranged in closest packing. For the diameter of the spheres 2.3×10^{-8} cm [1]) has been taken.

Fig. 2 shows the course of the 4 adsorption isotherms measured. The measurements were continued for the lowest three temperatures till con-
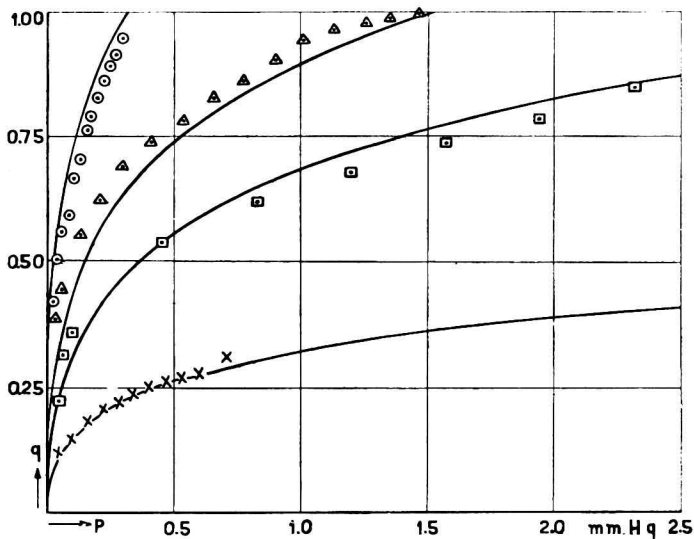

Fig. 2.

densation set in. The vapour pressures then observed were somewhat larger than CROMMELIN and GIBSON's [2]) values. Leaving open the question whether this difference is real or a consequence of the small admixture of helium referred to in § 3, we calculated the "saturation densities" mentioned in table I and used for checking equation (3) of § 5 with our values, these being the saturation pressures valid for the gas we experimented on.

b. Fig. 2 shows in the first place how the amount of covering of the wall in the range of unsaturated gas density everywhere remains below that by a complete monomolecular layer. This agrees with what LANGMUIR (l.c.) and after him other observers found in cases in which we have to do with a purely physical phenomenon and the gas has no prominent dipole character. It further shows that complete monomolecular covering seems to be reached near the saturation density.

It must be remarked that this conclusion depends on two assumptions, *viz.* that of closest packing arrangement of the adsorbed layer, and that of perfect smoothness of the wall, which probably are not quite correct. There may be some small space between the adsorbed atoms on one hand, the real wall surface probably will be some percentages larger than the geometrical surface we have reckoned with on the other hand. These two circumstances will partly cancel one another.

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[1]) A. O. RANKINE, Phys. Zs. 11, 745, 1910.

[2]) C. A. CROMMELIN and R. O. GIBSON, These Proc., 36, 362, 1927; Comm. N°. 185b.

Apart from this uncertainty especially the two point series corresponding to $T = 14.45°$K. and $T = 15.86°$K. point to the remarkable coincidence we mentioned.

§ 5. *Discussion.* *a.* These adsorption measurements were performed on glass with a view to gas thermometry. From a theoretical standpoint glass is, notwithstanding its smooth surface, not a very appropriate adsorbent, because of the very inhomogeneous structure of its surface. A further research on the adsorption of noble gases, and jointly of dipole gases, by glass covered with a monomolecular gas or with a metallic layer may be considered to be of very great importance for theory.

b. The inhomogeneous structure of the surface joined to the fact that glass is a non-conductor for electricity make, that a further elaboration of the electric theory[1]) of adsorption for it will have grave difficulties. The problem of the attraction between a noble gas atom and the **glass wall** will be very much like that of the VAN DER WAALS' forces.

We refrain from considering the nature of the adsorption forces and further discuss our results in terms of LANGMUIR's theory[2]).

For a wall with one kind of "elementary spaces" LANGMUIR deduces his well-known equation

$$q = \frac{c_1 \, c_2 \, p}{1 + c_2 \, p}, \quad \cdots \cdots \cdots \quad (1)$$

in which q is the fraction of the wall covered, p the gas pressure, c_1 and c_2 are constants. $c_1 \leqq 1 . c_2$ is proportional to the mean average life of the adsorbed molecules on the wall, which is supposed to be independent of the gas pressure.

A glass surface may be considered as consisting of different parts each with one particular kind of "elementary spaces". Then the equation of the adsorption isotherm will obtain a second member built up by a number of terms as in (1) each with its proper constants. At increasing pressure these parts will successively become saturated. Hence the mean average life for the surface as a whole will decrease with increasing pressure. Instead of trying such a complicated equation, which would possess many constants for our material, we confine ourselves to observing that equation (1) very well enables us to represent our adsorption isotherms for neon for values of $q < 0.5$, provided we express the dependence of the average life on the pressure by introducing c_2/q^2 instead of c_2.

So far our results may be considered to agree with LANGMUIR's theory.

c. For the range of larger degrees of covering, $q > 0.5$, our isotherms definitely show another course than might be expected from LANGMUIR's theory.

[1]) A. MAGNUS, l.c.
[2]) I. LANGMUIR, l.c.

As far as we know, gases as *Ne, Ar, He, N_2, O_2* and *H_2* have never been investigated before as to adsorption near to saturation, at least not on a perfectly smooth surface.

Coal as adsorbent is in this respect to be objected to, as capillary adsorption ought to be avoided for comparing with LANGMUIR's theory.

In our experiments capillary condensation could occur at very narrow strips of the exterior walls of the small tubes, where they are in contact with each other. Only for so far as the interspace between two tubes in contact has molecular dimensions, capillary adsorption can occur. Hence these strips are so narrow that their total surface may be neglected, even if covering with a multimolecular layer were supposed.

Our measurements for the range of larger degrees of covering point to a certain connection between the attainment of saturation in the adsorbed film and of saturation in the gas.

LANGMUIR's equations do not suppose this connection. This is a consequence of the fact that LANGMUIR neglects the average life of incident molecules on already adsorbed molecules. This may be practically right for small degrees of covering, it is questionable whether it is also right for larger amounts of covering. Neglecting this average life at larger gas densities is in fact equivalent to neglecting the VAN DER WAALS' forces between the molecules and the wall. In reaching saturation the VAN DER WAALS' forces, however, play an all important rôle.

Independently of the special theory we may form about gas condensation, we shall have to assume that when condensation begins groups of molecules will take up colliding molecules with a certain average life.

As it seems rather difficult to express this influence in an exact way, we tried to account for it by dividing p by $p_s - p$ (p_s referring to saturation pressure), so that equation (1), introducing also c_2/q^2 for c_2 as explained in *b*, changes to

$$q = \frac{c_1 c_2 p}{q^2 (p_s - p) + c_2 p}.$$

For the sake of simplicity we replaced, in the denominator, $c_2 p$ by $c_2 p q^2$. This change has only a small influence, as for small values of q p is very small, so that the first term in the denominator is by far preponderant, whereas for small values of $p_s - p$, so that the first term is preponderant, q approaches to 1.

Taking into account that for $p_s - p = 0$, $q = 1$, the formula may then be written as follows

$$q^3 = \frac{p}{k (p_s - p) + p} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

The curves in fig. 2 represent the isotherms calculated with

$$q^3 = \frac{p}{0,7 (p_s - p) + p} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

We recognize that this formula not only fairly well agrees with the experimental results for the individual isotherms, but that it also accounts in a satisfactory degree for the dependence of the adsorption on temperature.

Physics. — *Measurements on the adsorption of helium on glass at liquid helium temperatures.* By W. H. KEESOM and G. SCHMIDT. (Communication N⁰. 226b from the KAMERLINGH ONNES Laboratory at Leiden.)

(Communicated at the meeting of September 30, 1933).

Summary. The adsorption of helium on glass was investigated at liquid helium temperatures. The results can be represented fairly well by the formula

$$q^4 = \frac{p}{0.26\,(p_s - p) + p}.$$

One measurement on the adsorption of hydrogen at 15.1°K. was made.

It was tried to make helium thermometer measurements below 1°K. possible by adding some neon. This procedure did not lead to success.

§ 1. *The measurements* of the adsorption of helium on glass were made after the same method as those of the adsorption of neon dealt with in the preceding paper [1]). They are somewhat less accurate because of the large thermomolecular pressure differences that occurred in these experiments. These pressure differences were measured in the same way as described in § 3 of the preceding paper.

Dimensions of the apparatus:

volume thermometer bulb 4.356 cm³,

supplementary surface of glass capillaries 133 cm²,

internal diameter thermometer capillary 1.20 mm.

The whole apparatus was made of Thüringen glass.

§ 2. *The results* have been collected in table I.

p represents the gas density, measured as the pressure the gas would exert in the same volume at the temperature 4.22°K. q is the quantity of gas adsorbed divided by the quantity necessary to cover the glass wall with a monomolecular layer of helium atoms arranged as spheres of diameter 1.9×10^{-8} cm [2]) in closest packing.

Each set of values in table I is an average of 3 to 4 observations.

The results have been represented in fig. 1.

It appears that the behaviour of helium is quite similar to that of neon (cf. fig. 2 of Comm. N⁰. 226b).

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[1]) W. H. KEESOM and G. SCHMIDT, These Proceedings **36**, 825, 1933, Comm. Leiden. N⁰. 226b.

[2]) W. SUTHERLAND, Phil. Mag. (6) **19**, 25, 1910.