This 'value[1]) is smaller than that found by direct measurement
at the smallest velocity of vaporization[2]): 110.2. It is possible that
this result indicates that the precautions taken to prevent condensa-
tion of the vaporized hydrogen within the calorimeter have not been
sufficient. In fact at a velocity of vaporization twice as great as
that at which the value mentioned above was found smaller values
were obtained, viz. 108.5 and 109.3 at 76.1 and 77.75 cm. pressure
respectively.

Physics. — "*Vapour pressures at very low reduced temperatures.
II. The vapour pressure of carbon dioxide in the range
from* — 140° *C. to about* 160° *C.*" By Sophus Weber. Com-
munication No. 137c from the Physical Laboratory at Leiden.
(Communicated by Prof. Kamerlingh Onnes).

(Communicated in the meeting of September 27, 1913).

§ 1. In these measurements the heated-wire manometer described
before was used[3]); it was calibrated by the aid of a set of pipettes
as shown in fig. 1. The manometer is sealed to the vessel P_3 at J
and is placed, together with P_1 and P_2 in a waterbath, in which
a temperature of about 20° C. is maintained by means of a thermostat.
This temperature is read on a mercury thermometer. The electric
connections are the same as in fig. 4 of the first paper. In order
to keep back mercury vapour or other vapours which might originate
in P_3 the tube I the volume of which is only 1 °/₀ of the whole
volume was placed in alcohol cooled to about — 100° C. by the aid
of liquid air. In a high vacuum the vapours given off by the grease
of the stopcocks will be condensed in I. I have tried to prevent
this flow of vapour to I while retaining the taps by interposing at

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1) It may be noticed that this value nearly coincides with that calculated from the
vapour pressure measurements of Dewar (cf p. 441 note 1). The difference which
shows the value derived from the vapour pressure measurements of Travers and
Jaquerod (cf. p. 441 note 1) is due to the diverging course of their vapour
pressure curve, cf. p. 444 note 1. [Added in the translation]

2) Cf. p. 441 note 1.

3) H. Kamerlingh Onnes and Sophus Weber, Comm. N⁰. 137b (June 1913).

Fig 1.

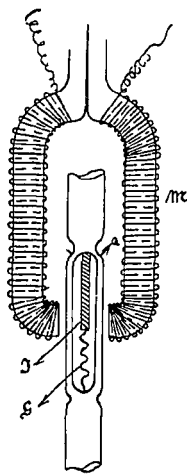G and H glass valves as introduced by KAROVODINE in TÖPLER-HAGEN's mercury pump.

Fig. 2 shows one of these valves, a is a ground surface. Inside the glass tube a small piece of iron is fastened: without a current through the electro-magnet M the communication is open to the gas; when the current is closed the vapours can only diffuse through the narrow interstices left open at a. The measurements seem to confirm that by the use of these valves a better vacuum may be obtained.

The calibration was performed in the following manner. By means of the high-pressure taps D and C some carbon dioxide was taken from the cylinder A containing carbon dioxide which had been thoroughly dried and distilled several times. This gas was solidified in E by means of liquid air and subsequently strongly exhausted with a GAEDE-pump. It was then distilled into pipette p_1 and the pressure read with the manometer F. The pipettes P_1, p_2 and P_2, which communicated with the heated-wire manometer were evacuated and the vacuum was measured with the aid of this manometer, which had been previously compared with an absolute manometer. The gas in p_1 was then distributed over p_1, P_1, and p_2. If stop-cock 3 is now closed and 4 opened, the gas in p_2 is distributed over p_2 and P_2, by which the pressure in P_2 increases by a known amount. By connecting p_2 with P_1 and with P_2 successively the pressure in P_2 again increases by an amount which is known, at least if the dimensions of the apparatus are known. They were:

Fig. 2.

$$p_1 = 13.997 \text{ cm}^3$$
$$P_1 = 2108.15 \quad \text{,,}$$
$$p_2 = 13.464 \quad \text{,,}$$
$$P_2 = 2555.7 \quad \text{,,}$$

Each time when the pressure had been raised by a known amount the loss of heat of the WOLLASTON-wire under definite conditions was measured. The following table may serve as an instance of the calibration: q is proportional to the loss of heat per second and p is the pressure in baryes computed by means of the system of pipettes. The initial pressure is taken as zero in the table; in reality it amounted to 0.029 baryes.

TABLE I	
p	*q*
0.000	0.6731
5.059	0.8019
10.099	0.9292
15.120	1.0551
20.122	1.1804
25.106	1.3044
30.070	1.4279
35.016	1.5305
39.943	1.6724
44.851	1.7932
49.740	1.9132
54 611	2.0332
59.464	2.1522

§ 2 After the calibration was completed the manometer was put into connection with a vapour pressure tube. This tube was of the form described in the previous communication. The measurements were conducted in the following manner. The apparatus was first exhausted as far as possible and was allowed to stand for some days, until the walls did ·not give off any more air. The vapour pressure tube which was placed in a cryostat together with a thermometer and a stirrer was then successively surrounded by ethylene, methane and oxygen, and the vacuum was measured at temperatures between —130° C. and —180° C. Carbon dioxide was then distilled into the apparatus and the vapour pressure measured at a series of temperatures. The difference between the two readings at each temperature after correcting for the thermal molecular pressure gives the vapour pressure of carbon dioxide.

In order to be able to obtain the corrections for the thermal molecular pressure it is necessary to work with different tubes suitably chosen. In this investigation two tubes were used, tube I with a diameter of 1.75 cm. and tube II of 0.563 cm.

The results of the measurements are contained in table II

TABLE II				
Pressure				
Temp. $T-273.09$	Measured tube I	Measured tube II	I corr.	II corr.	Calculated according to NERNST
—134.67	1430.6	1430.6	1430.6	1430.4	1429.9
136.78	1001.2	1002.8	1001.2	1002.5	1002.0
138.69	720.0	720.6	719.9	720.2	719.3
140.63	509.2	510.8	509.1	510.2	508.7
143.07	324.7	323.9	324.6	323.1	324.2
145.44	207.0	204.2	206.8	203.1	206.70
148.27	117.72	119.7	117.42	118.0	117.30
151.46	48.42	50.30	47.90	47.86	47.84
155.00	28.33	30.65	27.70	28.21	27.56
158.55	12.92	14.09	12.34'	12.12	12.00
159.72	9.82	10 72	8.66	8.94	9.015
161 39	6.74	7.50	5.85	6.00	5.942
163.19	4.43	4.99	3 75	3.77	3.737
164.03	3.63	4.07	3 03	2.98	2.993
168.83	1.222	1.288	0.806	0.797	0.790

The first column contains the temperature as determined by means of a calibrated Pt.-thermometer. The second and third give the results of the measurements with the two tubes expressed in baryes, the fourth and fifth the same numbers after correcting for the thermal molecular pressure. For the measurements between —150° and —162° these corrections are somewhat uncertain, as they have been determined experimentally for hydrogen and oxygen only. Moreover the tubes had not been chosen as favourable as possible, as will be clear from the following.

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The corrections are calculated by means of KNUDSEN's formulae [1]. In the previous communication it was shown that with the degree of accuracy of our measurements these formulae may be considered as correct, if the region where approximately $1 < \dfrac{\lambda}{2R} < 10$ is excluded. If BREITENBACH's observations on the viscosity of carbon dioxide are extrapolated by means of SUTHERLAND's formula [2] it may be concluded that the corrections cannot be computed in the range between 25 and 3 baryes for the wide tube and between 75 and 8 baryes for the narrow tube. Supposing that the mean free path is known with sufficient accuracy it will be seen that between 25 and 8 baryes there is a range for which the correction cannot be calculated. An additional tube of say 1 mm. diameter ought to have been used.

It appears further that below 3 baryes there is a range of pressures, where the correction can be found for both tubes. With the formula which holds for this range the mean free path may be determined by eliminating the unknown vapour pressure. The result of this calculation is found to agree within the limits of accuracy of the observations with the mean free path as calculated with SUTHERLAND's formula. In table II this shows by the close agreement between the vapour pressures under I corr. and II corr.

The conclusion seems therefore justified that the mean free path of carbon dioxide is known with sufficient accuracy at these temperatures, and that the corrections may be deduced by means of KNUDSEN's formulae with the exception of the range between 25 and 8 baryes.

Leaving this range out of account in the mean time we will now discuss the formulae for those ranges where in our opinion they are still applicable.

$$(1). \quad \frac{2R}{\lambda} > 10.$$

In this range we use the following formula theoretically deduced by KNUDSEN.

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[1] MARTIN KNUDSEN. Ann. der Phys. 31 (1910), p. 205, 633 ; 33 (1910), p. 1435.

[2] The extrapolation by means of SUTHERLAND's formula is probably allowable in this case, as the range of reduced temperature is comparatively small. Over larger ranges of reduced temperature SUTHERLAND's formula does not appear to be applicable (H. KAMERLINGH ONNES C. DORSMAN and SOPHUS WEBER. Comm. N⁰. 134a March 1913).

$$\frac{dp}{dT} = \frac{0.00139 \dfrac{1 + \dfrac{c}{273}}{1 + \dfrac{c}{T}} \eta_0 \sqrt{\varrho_0}\, k_1}{R + 32.07 \dfrac{\left(1 + \dfrac{c}{T}\right)\sqrt{\varrho_0}}{\left(1 + \dfrac{c}{273}\right)\eta} R^2 \dfrac{p}{T} k_2} \quad \ldots \ldots \quad (I)$$

The meaning of the symbols is the same as in KNUDSEN's paper. According to the theory the constants k_1 and k_2 are independent of the nature of the gas. Experimentally this formula has been confirmed for hydrogen and oxygen, and k_1 and k_2 appear actually to be independent of the nature of the gas. The equation which may be integrated in a fairly simple manner loses its validity for small values of $\dfrac{2R}{\lambda}$. For carbon dioxide the formula was used with the values of k_1 and k_2 which were found from the measurements with hydrogen and oxygen. As shown by Table II the numbers under I corr. and II corr. agree well with each other which may be looked upon as a partial confirmation of the underlying suppositions. Fig. 3 gives a graphic representation of $\dfrac{dp}{dT}$ according to the different formulae. The abscissae give the pressures in baryes, the ordinates $\dfrac{dp}{dT}$ for the tube with $2R = 0.563$ cm. Curve 1 represents the relation according to formula I. For the corrections the formula has not been used, when $\dfrac{2R}{\lambda} < 10$; it depends, however, on the degree of accuracy required, where the limit has to be taken.

(2). $\dfrac{2R}{\lambda} < 1$.

In this case the following formula was used for $\dfrac{dp}{dT}$:

$$\frac{dp}{dT} = \frac{1}{2} \frac{1}{1 + \dfrac{2R}{\lambda}} \frac{p}{T}$$

where p and λ are connected by the relation $p \cdot \lambda = \text{const.}$; this constant is determined by the viscosity corresponding to the temperature T.
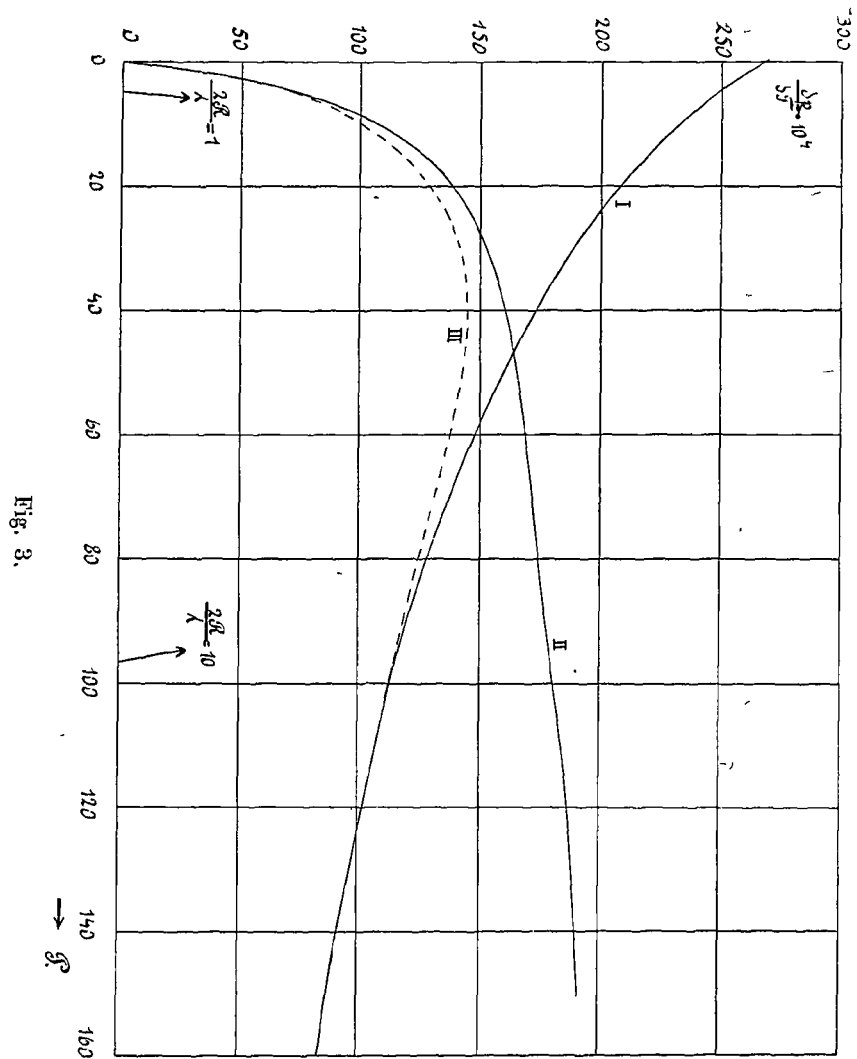
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Fig. 3.

For sufficiently small values of $\dfrac{2R}{\lambda}$ the formula reduces to

$$\frac{dp}{dT} = \frac{1}{2} \cdot \frac{p}{T} \quad \text{or after integration} \quad \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$$

The limit for the application of formula II has been taken at $\dfrac{2R}{\lambda} = 1$, which gives about the same accuracy as in the former case. The relation between p and $\dfrac{dp}{dT}$ according to formula II is also given in fig. 3.

(3). $1 < \dfrac{2R}{\lambda} < 10.$

In this region the formulae can probably only be used as rough approximations. Curve *III* in fig. 3 has been obtained by reducing the observations for hydrogen and oxygen to carbon dioxide by means of the law of corresponding states. The values given by *III* have been used in this range for calculating the corrections. The results under I corr. and II corr. agree fairly well with each other. The observations are, however, not sufficient to draw conclusions with regard to the value of thermal molecular pressure in this intermediate region.

This region has, therefore, not been sufficiently studied as yet and new measurements in this range would be of the greatest interest.

In table II column 5 under "calc. according to NERNST" the pressures are given calculated by the aid of NERNST's formula. In the former paper use was made of the formula with the values of the constants found by FALCK [1]), viz.

$$\log p = - \frac{6000}{4.571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0.00913}{4.571} T + 3.1700 \quad . \quad (I)$$

In order to obtain a satisfactory agreement at higher pressures the constants had to be slightly modified as follows

$$\log p = - \frac{6007.9}{4.571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0.009008}{4.571} T + 3.1700 \quad . \quad (II).$$

p is here expressed in atmospheres.

The coefficient of $\log T$ and the chemical constant are unchanged, and the other two constants have been only slightly altered. This alteration can have no influence on FALCK's theoretical deductions. The very low vapour pressures which we measured before with the absolute manometer are also unchanged, as the term proportional to T has but little influence in that region. In that case NERNST's formula reduces to the vapour pressure formula according to KIRCHHOFF-RANKINE-DUPRÈ [2]).

It can hardly be expected that formula *II* should give good agreement at temperatures much higher than those given in table II. At higher temperatures FALCK finds greater deviations which, however, he considers to be due to errors of observation. I have

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[1]) F. FALCK: Phys. Z. S. 1908, p. 433.

[2]) H. KAMERLINGH ONNES und W. H. KEESOM: Die Zustandsgleichung Leiden Comm. Suppl. N⁰. 23, pag. 300.

made only one measurement at temperatures higher than those given in table 2.

Temperatures $T - 273.09$	p cm. Hg	Calc. by form II.
— 129.29	0.3943	0.2536
— 129.28	0.3948	0.2539

Although this measurement is the only one it may be considered sufficient together with the observations by ZELENY and SMITH[1] to infer a considerable deviation from the formula at this temperature.

In conclusion I am glad to record my gratitude to Prof. H. KAMER-LINGH ONNES for his kind assistance and his ever ready interest in my work.

Physics. — *"On the magnetization of ferromagnetic substances· considered in connection with the assumption of a zero-point energy".* By Dr. W. H. KEESOM. Supplement N⁰. 32a to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 27, 1913).

I. On the spontaneous magnetization.

§ 1. *Introduction.* NERNST[2] was the first who suggested that the quantum-theory has to be applied also to the rotations of gas molecules. Since that time the measurements by EUCKEN[3] and those by SCHEEL and HEUSE[4] have confirmed the anticipation expressed by KAMERLINGH ONNES[5], that the decrease which according to that application is to be expected in the specific heat at constant volume of hydrogen in the gas state, would already occur at realisable temperatures. By this result they have demonstrated very clearly the necessity of that application. At the same time they have given

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[1]) ZELENY u. SMITH. Phys. Z. S. pag. 667, 1906.

[2]) W. NERNST. ZS. f. Elektrochem. 17 (1911), p. 270 W. NERNST and F. A. LINDEMANN, ibid. p. 825. Cf. also A. EINSTEIN, Rapports conseil SOLVAY 1911, p. 432.

[3]) A. EUCKEN. Berlin Sitz.-Ber. 1912, p. 141.

[4]) K SCHEEL and W. HEUSE. Berlin Sitz.-Ber. 1913, p. 44. Ann. d. Phys. (4) 40 (1913), p. 473.

[5]) Rapports conseil SOLVAY 1911, p. 301. ZS. f. Elektrochem. 17 (1911), p. 826. Cf also H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N⁰. 23, § 57 f.