## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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Physics. — "Vapour pressures of substances of low critical temperature at low reduced temperatures. I. Vapour pressures of carbon dioxide between — 160° C. and — 183° C. By H. KAMERLINGH ONNES and SOPHUS WEBER. Communication N°. 137b from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of June 28, 1913).

§ 1. Introduction. The knowledge of the vapour pressures of substances of low critical temperature at low reduced temperatures has recently obtained special importance<sup>1</sup>). The gradual transformation shown by the reduced equations of state for various substances, when ordered according to their critical temperature, manifests itself in particular in the gradual transformation of the reduced vapour pressure curves, and the deviations from the law of corresponding states, which show themselves clearly in this transformation and are connected with NERNST's heat-theorem, have acquired increased importance by the connection with PLANCK's theory of energy-quanta.

We have therefore undertaken a series of determinations of vapour pressures for substances of low critical temperature at lower temperatures than in previous determinations. The measurement of the very low vapour pressures with which we are concerned in this case forms a separate branch of research. In measuring the pressure in a space at ordinary temperature, connected by a tube with the space, where the vapour and liquid or solid are in equilibrium at a known low temperature, correct results can only be arrived at, if due regard is paid to the theory of the thermal molecular pressure.

KNUDSEN<sup>2</sup>), who has developed this theory, has shown that, when a temperature gradient exists along a closed tube containing a gas in equilibrium, there will in general be a pressure difference between the ends of the tube, such that the higher pressure is observed where the temperature is higher. The magnitude of the difference depends on various -circumstances, specially on the ratio of the radius of the tube R to the free path of the gas molecules  $\lambda$ . In the limiting

<sup>2</sup>) MARTIN KNUDSEN: Ann. d. Phys Bd. 31 p. 205 1910.

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<sup>&</sup>lt;sup>1</sup>) For the literature and a discussion of the questions referred to here, see: H. KAMERLINGH ONNES and W. H. KEESOM: Die Zustandsgleichung. Enc. d. math. Wissensch. V. 10. Leiden Comm. Suppl N<sup>0</sup>. 23.

cases, calling  $p_1$  and  $p_2$  the pressures,  $T_1$  and  $T_2$  the absolute temperatures at the ends, we have

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 $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \text{ for } \frac{R}{\lambda} = \frac{1}{\infty}$   $p_1 = p_2 \text{ for } \frac{R}{\lambda} = \infty$ 

For intermediate cases KNUDSEN deduces more complicated formulae which may be applied over a wide range. As a rule the matter reduces itself to the application of a correction to one of the limiting cases. The application of the formulae is not allowed over the range defined by

$$1 < \frac{2R}{\lambda} < 10$$

When these limits are exceeded, the accuracy very soon falls below  $1^{\circ}/_{\circ}$ . It is necessary, therefore, to avoid the above range in the measurements by a suitable choice of the tubes connecting the evaporating surface with the measuring apparatus, and by changing them, when occasion arises. When this is found to be impossible, the measuring apparatus will have to be kept at a temperature but little higher than that of the liquid or the thermal molecular pressure will have to be measured experimentally or a different method altogether will have to be resorted to <sup>1</sup>).

In the range where the measurements can be corrected to the limiting cases by means of the more complicated formulae referred to it may occur, that the corrections cannot be applied for a given tube owing to the free path being unknown and that this quantity cannot be found with sufficient accuracy by extrapolation: in that case the object can be attained by means of measurements with two different tubes suitably chosen, so as to eliminate the pressure and obtain data for the calculation of the free path, which can then be introduced into the formulae.

The pressures which we wished to measure lie between 0.02 baryes and 1 mm. The highest of these might still have been measured with a MAC LEOD gauge, but for the lower ones this method is not applicable owing to the possibility of mercury distilling over at the low pressure to the cold substance. We have therefore used KNUDSEN'S heated wire gauge <sup>3</sup>) between 1 mm. and 0.01 mm. and KNUDSEN'S absolute manometer <sup>3</sup>) between 0.001 mm. and 0.01 mm.

<sup>&</sup>lt;sup>1</sup>) E. g. KNUDSEN's method of molecular effusion through a small orifice, in which the amount of vapour passing through is measured instead of the pressure.

<sup>&</sup>lt;sup>2</sup>) MARTIN KNUDSEN, Ann. d. Phys. Bd. 32, p. 809, 1910.

<sup>&</sup>lt;sup>3</sup>) MARTIN KNUDSEN, Ann. d. Phys. Bd. 35, p. 389, 1911,



wire is connected to M, the upper one passes through the screw Eand is clamped with the screw e. By means of E M can be made exactly parallel to the flat sides of B.

A is a platinum wire which prevents the mica plate falling down when the apparatus is inverted.

The two windows  $O_1$  and  $O_2$  serve for the reading of the rotation of M: for this purpose the outer edge of the mica plate is observed in a LEITZ reading microscope with eye-micrometer. The temperature of the german-silver tube is read on a thermometer which is in metallic connection with it and protected from radiation by means of the tube H.

The tube B is held in the glass vessel (fig. 2) by the springs S. The dimensions of the various parts of the apparatus were as follows : area of  $V_1$  9.030.1.18 cm<sup>2</sup>.

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§ 2.

9.005 . 1.20 cm<sup>2</sup>.

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distance between the centres of $V_1$ and $V_2$	
(arm of couple)	1.190 cm.
length of mica plate	12.70 cm.
width ", ", "	3.117 cm.
moment of inertia	1.415 er. cm <sup>2</sup> .
time of oscillation (full period)	3.53 sec.
agnification of microscope 4 num - 87 5 scale	divisions on micro

magnification of microscope 4 num = 87.5 scale divisions on micrometer.

In fig. 2 is shown the manner in which the manometer was mounted.





The tube B is placed inside a glass tube which is provided with a water-jacket W; through W hot or cold water can be passed,

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as required, by means of the pinching screws  $K_1$  and  $K_2$ . The temperature of the jacket is read on the thermometer  $T_2$ .

The vapour pressure tube R which is sealed to the manometer tube, bent over and closed at the bottom, is placed in a cryostat with a calibrated resistance thermometer which gives the temperature of the evaporating surface. The diameter of the tube R was 1.71 cm.

The best method of securing an even temperature in the cryostat is stirring with a "pump-stirrer", in this case however, as the smallest vibrations disturb the readings of the manometer, preference was given to the use of a stream of vapour-bubbles evolved by local heating with an electrically heated wire.

§ 3. Calibration of the absolute manometer. In the first place it was necessary to consider for what range of pressures the manometer may be used as an absolute instrument. In the second place seeing that the distance of the mica-plate to the windows V cannot be treated as infinitely small and the sensibility can thus only be calculated approximately, the value of a scale reading at given difference of temperature between outer wall and mica plate must be expressed in baryes.

According to KNUDSEN the force per  $\operatorname{cm}^{v} K$  on the plate in the lumiting case, when the mutual collisions of the molecules may be disregarded, is given by

$$K = \frac{1}{2}p\left(\left| \frac{\overline{T_1}}{\overline{T_2}} - 1\right|\right),$$

where p stands for the pressure,  $T_1$  and  $T_2$  for the temperatures of plate and wall respectively.

As regards the condition under which this formula may be used, it is found that in order to reach an accuracy of  $\frac{1}{2}\frac{\theta}{\theta}_0$  in the final result, the free path must be at least ten times the diameter of the tube. The range of the manometer is thus different according to the gas used. For carbon dioxide according to BREITENBACH's measurements of the viscosity at 20°  $p.\lambda = 7.4$ , if p is expressed in baryes and  $\lambda$ is the mean free path in cms. From this it follows that the range of our gauge reaches up to about 0.3 barye.

The range can also be determined by connecting the manometer with spaces, where known pressures are established, and ascertaining for what pressures the elongation remains proportional to the pressure. In any case it is necessary, with a manometer such as ours which, as we have seen, does not allow the calculation of the reduction factor from the dimensions of the apparatus, to make measurements for the determination of this factor. By extending the

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calibration to pressures at which the elongation is no longer proportional to the pressure (supposing the rotation in any case to be infinitely small) the apparatus can be made into a pressure-indicator for that range, instead of an absolute manometer.

For the purpose of the calibration the manometer was connected with a system of pipettes according to KNUDSEN<sup>1</sup>), for the description of which we refer to a subsequent paper<sup>2</sup>). The results are contained in the following table:

TABLE I. Calibration of the absolute manometer.					
Approximate pressure in baryes,	∆ abs. man.	∧ according to pipettes in baryes	$\frac{\triangle \text{ pip.}}{\triangle \text{ abs.M.}}$		
0.147 0.574 0.931 1.234 1.497 1.711	0.427 0.357 0.303 0.263 0.214	0.390 0.385 0.381 0.376 0.372			
0.056 0.170 0.283 0.393 0.500 0.605	0.114 0.113 0.110 0.107 0.105	0.1005 0.0996 0.0984 0.0972 0.0960	0.881 0.881 0.895 0.908 0.914		

The first column gives the pressures calculated according to the indications of the absolute manometer by the formula

$$\frac{1}{2} p\left(\left| \begin{array}{c} T_{s}'' \\ T_{1}'' \\ \end{array} - \left| \begin{array}{c} T_{s}' \\ \end{array} \right|^{2} = c \left(\alpha_{1} - \alpha_{2}\right)$$

1) MARTIN KNUDSEN, l. c.

<sup>&</sup>lt;sup>2</sup>) S. WEBER. Vapour-pressures etc, II. The vapour-pressures of carbon dioxide between  $-140^{\circ}$  C. and  $-160^{\circ}$  C. Comm. N<sup>0</sup>. 137*c*. The same pipettes have also been used for the calibration of a hot-wire manometer for the purpose of thermometric measurements, which will be discussed in future communications about experiments with liquid helium.

where  $T_{2}^{"}$  and  $T_{1}^{"}$  represent the temperatures of outer wall and mica plate (properly speaking tube *B*) respectively in the experiment at the ordinary temperature,  $T_{2}^{"}$  and  $T_{1}^{"}$  the corresponding temperatures in the experiment at higher temperature, *c* the value of the reduction factor calculated from the dimensions of the apparatus (as we have seen this calculation can only give an approximate value),  $\alpha_{1}$  and  $\alpha_{2}$  the two elongations. The second column gives the differences of the successive pressures, the third the same differences according to the observations with the pipettes.

In the first series the limits of proportionality are evidently far exceeded: it can therefore serve as a calibration of the manometer as a pressure-indicator. The second series shows clearly that at first the absolute manometer gives greater values for the pressures than the pipettes, which are however in a constant ratio to the latter, while later on its readings are lower than those of the pipettes, as might be expected '). It is also intelligible that our mancmeter gives higher readings in the beginning than the pipettes considering that the distance between the windows and the mica plate cannot be taken as small as compared with the width of the windows, so that parts of the movable mica plate outside the perpendicular projection of the windows will also be struck by molecules which proceed from the heated wall. This action along the edges owing to which c can only be approximately calculated was considerable in our case; its influence on the pressure follows immediately from the above calibration numbers: obviously c has to be replaced by  $\frac{1}{0.881}c =$ 

1.135 c.

§ 4. The measurements.

a. The manometer mounted as in fig. 2 was then exhausted for a long time under strong heating to  $300^{\circ}$  C.: for this purpose it was joined to a GAEDE molecular airpump, for the loan of which we are indebted to the kindness of LENBOLDS.Nachf. of Cologne, which we here gratefully acknowledge. As appears from the measurements communicated below it is possible to use this excellent, reliable and easily worked instrument continuously at pressures of 0,007 barye without the least trouble. After having been connected to the pump at the temperature mentioned for about a day the manometer ceased to give off gas. The vacuum had become constant. The small remaining pressure was thereupon measured, while the vapour

<sup>&</sup>lt;sup>1</sup>) DEBIJE (Physik, Zs. 1911, p. 1115) has tried to represent this behaviour by a formula of approximation.

pressure tube R was first placed in liquid oxygen and afterwards in methane of different temperatures. It appeared that the vacuum remained constant within the limits of accuracy and was independent of the temperature of the vapour pressure tube<sup>1</sup>). Carbon dioxide carefully dried and repeatedly distilled in vacuo was now introduced through a side tube into the tube R, which was cooled with liquid air. When a sufficient quantity had passed over, the apparatus was again connected to the molecular pump and evacuated during a considerable time. The manometer was then sealed off from the pump at a and the pressure measured, while R was surrounded with oxygen boiling under reduced pressure. It was found that the vacuum was the same as before the introduction of carbon dioxide, from which it follows that at  $-205^{\circ}$  C. the vapour pressure of carbon dioxide must be smaller than 0,005 barye. A difference of 0,002 barye could be clearly detected and the influence of vibration was also just below this value; 0,005 barye could thus not escape observation.

 $\beta$ . As a rule the further observations were mode in the following manner: first the manometer is brought approximately to temperature-equilibrium, and the thermometers  $T_2$  and  $T_1$  are read; warm water is then made to pass through  $K_1$  until a suitable temperature is reached;  $T_2$  and  $T_1$  are again read and the reading on the eyemicrometer is taken. Finally cold water is let into  $K_2$ . until  $T_1$  has about assumed the original temperature, after which a second observation is made at the same temperature.

The calculation is made in the manner explained in section 2.

As described the vacuum was measured before carbon dioxide was admitted, R being at temperatures between — 160° C. and — 200° C., when 0,007 baryes was found for the pressure. After sealing off the same value 0,007 baryes was found. A complete series of observations was then taken, first with methane and then with oxygen in the cryostat. The apparatus was then left standing for a few days, after which a new series of observation was taken. In the mean time the vacuum appeared to have risen to 0,016 barye. If this change is taken into consideration the two series agree well with each other.

In table II the two sets of measurements are combined. The figures in the  $3^{rd}$  column are derived from those in the  $2^{nd}$ 

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<sup>&</sup>lt;sup>1</sup>) The radiation-pressure did not amount in our case to more than  $0.05 \cdot 10^{-3}$  barye, when the wall was at  $100^{\circ}$  C.

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TABLE II. Vapour pressures of carbon dioxide at temperatures between — 183°.0 and — 167°.04.					
Temp. T-273°.09	Pressure observed in baryes diminish- ed by residual pressure	Vapour pressure in baryes.	Calculated according to NERNST.		
- 183.0	0.015	0.008	0.0067		
179.60	0.047	0.026	0.0241		
175.37	0.179	0.106	0.1012		
171.01	0,620	• 0.404	0.4083		
168.83	1.143	0.791	0.7782		
167.04	1.780	1.310	1.297		

by correcting for the thermal molecular pressure. This was done by means of the formula given by KNUDSEN:

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}} \cdot \frac{1}{1 + \frac{2R}{\lambda}}$$

where  $p_1$  and  $p_2$  are the measured pressure and the real pressure respectively,  $T_1$  and  $T_2$  the corresponding temperatures, 2R the diameter of the vapour pressure tube and  $\lambda$  the mean free path calculated from p! = 4. This relation was thus also applied in conditions, where the mean free path is not well represented by SUTHERLAND'S formula<sup>1</sup>): this may, however, be considered allowable

in view of the small influence of the term  $\frac{2R}{\lambda}$ .

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It will be seen that the main term of the correction is large: but its value is accurately known and is in no way connected with the additional correction for  $\lambda$ . The latter is only of importance in the last measurements.

It is possible by a suitable choice of the radius of the vapour pressure tube R to make the additional correction so small, that it may be entirely neglected. It is our intention to do this in future experiments in order to become entirely independent of the small

1) The circumstance that in the exponential form the same factor is here used for the residual pressure, although the substance to which this pressure is due, is unknown, is of no importance within the limits of accuracy of the experiments. uncertainty arising out of this cause at present. In those experiments a little more time will have to be allowed for the setting in of the equilibrium pressure.

## § 5. Determinations with the hot-wire manometer.

With regard to the choice of the shape and dimensions of the vapour-pressure tube R, used in the measurements with the absolute manometer, the question arises whether sufficient account has been taken of two causes of disturbance which may influence the results obtained. The tube being long cannot in itself be considered a sufficient precaution to exclude radiation from above, by which the temperature-equilibrium of the evaporating surface is rendered uncertain, furthermore it has to be ascertained, whether the surface of the liquid bath may possibly be at a lower temperature than the bath at the spot, where the temperature is measured <sup>1</sup>).

In view of the degree of accuracy of the measurements with our absolute manometer the errors arising out of these causes of disturbance may be neglected.

With our hot-wire manometer the accuracy which could be attained in the region of less low pressures, at which measurements were also intended, was considerably higher. In designing the vapour pressure apparatus intended for the measurements with this manometer the possible influence of the aforesaid causes of error was therefore carefully avoided.

The hot-wire manometer which we used is represented in fig. 3. It consists of a Wollaston-wire (0.005 mm. in diameter and about 10 cm. long), stretched in a frame of platinum wire abc which forms at the same time the one electrode of the current. The second electrode e is insulated from abc by means of glass. The Wollaston-wire is fastened between b and d.

The dimensions are so chosen, that a pressure of 1 barye can be measured with great accuracy. This is the case when the diameter of the wire is small compared with the mean distance described by the molecules since their last collision: for as long as this condition is satisfied, the loss of heat by the wire may be taken approximately proportional to the density (or the pressure) of the gas. Owing to a deviation from proportionality, which is due to the heat flowing

<sup>&</sup>lt;sup>1</sup>) Comp. KAMERLINGH ONNES and BRAAK, Comm. N<sup>0</sup>. 107a. Even after 6 hours there was no sign whatsoever of a distillation of carbon dioxide at the bottom of R to the neighbourhood of the level of the liquid in the bath.



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off at the ends of the wire, a calibration is required. For this purpose the pressure was determined by means of the set of pipettes referred to before. The loss of heat is measured as follows. The wire forms one of the arms of a WHEATSTONE bridge (fig. 4); the corresponding arm has a resistance approximately equal to that of the wire, when it is heated to the definite temperature, which has been chosen with a view to the sensibility (in our 'case 86 degrees above 20° C.): it is kept at this temperature by regulating the main current. The two other arms have equal resistance (chosen in connection with the galvanometer resistance). The P. D. at the ends of a portion of one of these resistances is measured with a potentiometer free of thermo-effects: this gives the necessary data for the computation of the loss of heat.

The calibration was carried out with the set of pipettes mentioned above. Fig. 5 gives the two

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vapour pressure tubes. They were partly doublewalled; the walls are sealed together at the top and free at the bottom.

Where the external tube ends, the inner tube becomes narrower and is bent round in a spiral finishing up in a small bulb; this bulb is placed at the level of the middle of the thermometer. In the space between the two walls of the tube a wire is inserted which can be electrically heated, so as to secure, that the bulb is the coolest place of the vapour pressure tube. The object of the spiral is to compel the molecules which come in from above to collide a number of times with the wall before reaching the bulb. That part of the tube cannot contribute to the thermal molecular pressure, as it is practically at the same temperature over its entire length.

We have made a series of observations for carbon dioxide with this apparatus <sup>1</sup>).

We confine ourselves here to those measurements which give at the same time a check on the last measurements with the absolute manometer contained in Table 2. The results were as follows:

TABLE III. Vapour pressure of carbon dioxide at about — 168°.				
Тетр. <i>Т</i> — 273°.09 К.	Pressure in baryes.	Vapour pressure in baryes.		
	Vapour pressure tube I 2R = 1.57 cM.			
- 168.82	1.222	0.806 -		
	Vapour pressure tube II 2R = 0.563 cM.			
— 168.82	1.288	0.797 、		
- 167.04	2.098	1.313		

The last value will be seen to agree well with those obtained with the absolute manometer, while the first appears a little 'too

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<sup>&</sup>lt;sup>1</sup>) The measurements at higher temperatures are dealt with in the next communication: S WEBER The vapour pressures of carbon dioxide between  $-140^{\circ}$  C. and  $-160^{\circ}$  C.

high. We are uncertain as to the cause of this difference: most probably it is due to an uncertainty in the temperature with the absolute manometer.

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It is of special interest to compare these observations with NERNST's formula. The fourth column of Table II contains the pressures according to this formula, calculated with the constants which FALCK<sup>1</sup>) has determined with the data at his disposal. FALCK found the following expression

$$\log p \doteq -\frac{6000}{4,571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0,009983}{4,571} T + 3,1700$$

where p is the pressure in atmospheres.

The correspondence will be seen to be satisfactory considering the degree of accuracy of the observations. It does not look as if the constants could be materially improved.

Physics. — "On the equation of state of an ideal monatomic gas according to the quantum-theory." By Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 30a to the Communications from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

## (Communicated in the meeting of May 31, 1913).

§ 1. Introduction. Summary. DEBIJE<sup>2</sup>) has shown that agreement with the observations concerning the specific heat of solid substances can be obtained by modifying the theory of EINSTEIN<sup>3</sup>) in this sense, that the formula<sup>4</sup>) which PLANCK has given for the mean energy at the temperature T of a linear electrical oscillator is applied to the different principal modes of vibration of a solid.

It seems natural to apply the same principle to other material systems which can behave as an oscillator and hence to investigate the correctness of the consequences which follow from the hypothesis

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<sup>1)</sup> FALCK: Physik. Zeits. 1908, p. 433.

<sup>&</sup>lt;sup>2</sup>) P. DEBIJE. Ann. d. Phys. (4) 39 (1912), p. 789.

<sup>&</sup>lt;sup>3</sup>) For the literature see: H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. Nº. 23, § 74c.

<sup>4)</sup> DEBIJE makes use of the original formula of PLANCK, Wärmestrahlung, 1ste Aufl., p. 157. The more recent formula, Wärmestrahlung, 2te Aufl., p. 140, which differs from the first by the introduction of a zero point energy, leads to the same results as regards the specific heat as long as the frequencies do not depend upon the temperature. For processes in which the frequencies change, cf. P. DEBIJE, Programme for the WOLFSKEHL lecture, Physik. Z S. 14 (1913), p. 259, it can give diverging results for solids too.