

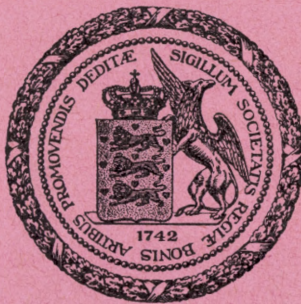
Det Kgl. Danske Videnskabernes Selskab.

Mathematisk-fysiske Meddelelser. **VIII**, 3.

THERMAL MOLECULAR PRESSURE IN TUBES

BY

MARTIN KNUDSEN



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

BIANCO LUNOS BOGTRYKKERI

1927

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Introduction.

If a gas is enclosed in two vessels communicating with each other by a tube, the gas will, as known, be in equilibrium if its pressure is of the same magnitude throughout. True, this condition of equilibrium only holds good if we disregard the differences in pressure produced by the effect of gravity. This we will do in the following. If the two vessels are given a different temperature, the condition of equilibrium will still hold good in many cases, even if the temperature is varied through the communication tube, and this fact is made use of, e. g. in the gas thermometer, it being a well-known fact that the gas in the manometer may have a temperature quite different from the gas in the thermometer bulb.

If, however, we employ the word equilibrium as a term for the state in which the amounts of the masses of gas found in the two vessels do not change any more if the temperature of the vessels remains unchanged, the condition of equilibrium mentioned may in certain cases become quite wrong. This was already shown by O. Reynolds¹, who by means of the kinetic theory derives the equation $\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}}$ as valid in the case of p_1 and T_1 being pressure and temperature respectively on one side of a porous plate, while p_2 and T_2 are the corresponding

¹ O. Reynolds, Phil. Trans. p. 727, London 1879.

quantities on the other side of the plate. Putting $p_1 = p_2$ and T_1 different from T_2 the gas will not be in equilibrium, there will be a flow of gas through the plate from the cold to the warm side. This flow of gas which Reynolds called "thermal transpiration" was demonstrated experimentally by Reynolds himself in experiments with plates of gypsum and meerschaum. The temperatures T_1 and T_2 were not, however, measured directly, so that Reynolds did not obtain a numerical confirmation of the equation given above. Such a confirmation I have achieved by means of a glass tube in which a magnesia plug had been firmly fixed, and the thermal transpiration was demonstrated in the following way.

I used a vessel holding from $\frac{1}{2}$ to 1 litre, and which was made of porous porcelain (a filtration bulb). The neck was closed with a rubber-stopper through which was passed a glass tube ending under a water surface. The gas in the bulb was heated by an electric current sent through a coil placed inside the bulb. The walls of the bulb being thus heated from the inside, and continually cooled on the outer side, a fall of temperature will take place in the porous wall, and this will cause gas to be sucked through the wall into the bulb. Gas bubbles will then rise through the surface of the water so that, in the course of a few minutes, more gas can be collected than the porous vessel holds. It will be noted too that the flow of gas will continue with constant velocity as long as the temperatures on the inner and outer sides of the walls are kept constant, and that the velocity increases when the heating current is increased or the cooling velocity of the bulb is augmented by blowing cold air on to it.

The condition of equilibrium stated by Reynolds is,

however, only valid when the effect of the collision of the molecules with each other as compared with the number of the impacts with the tube walls may be disregarded, or, in other words, when the cross-section dimensions of the tube are negligible compared with the mean free path λ of the gas molecules. For a cylindrical tube with the radius r the quantity $\frac{r}{\lambda}$ must thus be negligible compared with 1 if Reynolds' formula is to hold good.

If λ is negligible compared with r , the condition of equilibrium will, as known, be that the pressure is the same throughout the whole system whatever is the distribution of the temperature.

The case when λ is small but not negligible compared with r has been theoretically dealt with by MAXWELL¹ who made use of the results of KUNDT and WARBURG'S experiments on the slipping of the gases. By a consideration which I have formerly² explained I have arrived at a relation which formally agrees perfectly with Maxwell's. The constants found by me deviate somewhat from those found by Maxwell. A series of experiments previously made by me shows that the formulas in question are formally right, but that the constants found by experiments are again somewhat different from the theoretical ones, which is easily explained.

The theoretically found formula corroborated by experiment may be written as follows:

$$p_1^2 - p_2^2 = c(T_1^2 - T_2^2),$$

where p_1 and T_1 are the pressure and absolute temperature in one vessel, p_2 and T_2 the corresponding quantities in

¹ J. Clerk Maxwell, Phil. Trans. p. 231, London 1879.

² Martin Knudsen, Ann. d. Phys. Bd. 31, p. 214, 1910.

the other, while c is dependent on the radius of the tube and the mean free path λ_1 of the gas at a pressure of 1 bar. It may be expected too that c will in some degree be dependent on the temperature. For the cases when r is either negligible or very large compared with λ we have neither theoretical nor experimental investigations of the relation between p and T , yet a knowledge of this relation may be of great importance e. g. when the gas thermometer is to be used to measure the lowest temperatures that can now be produced.

In the following I shall give an account of a series of experiments performed by me for the purpose of learning more of this relation.

Experiments with the Gas Thermometer.

To solve the problem mentioned above I have tried using a gas thermometer and carrying out measurements

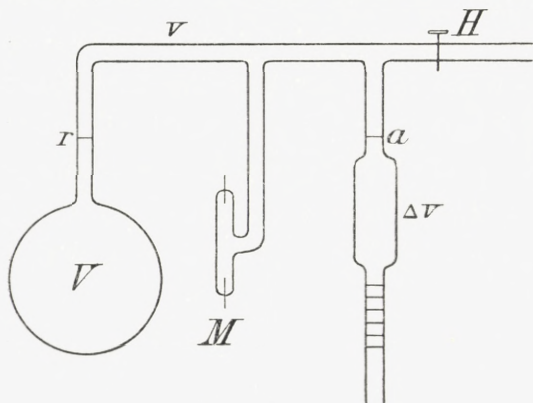


Fig 1

at constant pressure and varying volume. The glass apparatus is sketched in fig. 1. The volume V of the thermometer tube was measured, and likewise the radius r of the communication tube to the hot-wire manometer M ,

and the volume Δv of a pipette continued at the bottom in a graduated tube closed with mercury. H is a stop-cock through which hydrogen is introduced into the apparatus until the desired pressure is obtained.

Let us suppose that the whole apparatus has the absolute temperature T_1 and that the pipette is filled with mercury up to the mark a . There will then be the same pressure p_1 throughout the apparatus. Now the vessel V is heated to the temperature T_2 while the remaining part of the apparatus is kept at the temperature T_1 . The mercury is made to sink in the pipette until the manometer again shows the initial pressure p_1 . If the volume of the manometer and communication tube be designated v , and the new pressure in the heated vessel p_2 , the expression for the constancy of the mass of gas gives that

$$\frac{p_1 V}{T_1} + \frac{p_1 v}{T_1} = \frac{p_2 V}{T_2} + \frac{p_1 v}{T_1} + \frac{p_1 \Delta v}{T_1}$$

from which we get that

$$\frac{p_2}{p_1} = \frac{T_2}{T_1} \left(1 - \frac{\Delta v}{V} \right).$$

Here p_2 and p_1 designate the pressures in the communication tube with the radius r in the state of equilibrium in those places where the temperatures are T_2 and T_1 respectively, and p_1 and all quantities on the right side of the sign of equation being measured, the equation gives the sought relation between p_2 and p_1 .

We know that for large values of the pressure, that is to say abt. 1 cm. mercury pressure, we ought to find $p_2 = p_1$, and that for small values of the pressure, that is to say small values of $\frac{r}{\lambda}$, we ought to find small deviations from the equation $\frac{p_2}{p_1} = \sqrt{\frac{T_2}{T_1}}$. The first of these requirements was fairly well satisfied, which showed that the errors of observation were small. But from the second equation such

great deviations appeared that the method must be considered unsuitable.

The reason for this is that in each measurement great accuracy in the determination both of temperatures and volumes must be demanded, but of decisive importance are the adsorption phenomena that manifest themselves vigorously at lower pressures. This source of error I have not been able to eliminate, and my experiments seem to me to have shown that the gas thermometer is not suited for temperature measurements when the gas pressure in the vessel must necessarily be very low. Heating of the thermometer bulb and the use of Geräte glass somewhat reduced the error, though far from sufficiently.

Plan of the Experimental Investigation.

The method used for the final series of measurements was the following.

M (fig. 2) is a hot-wire manometer as previously described¹. By a series of glass tubes of unequal widths the

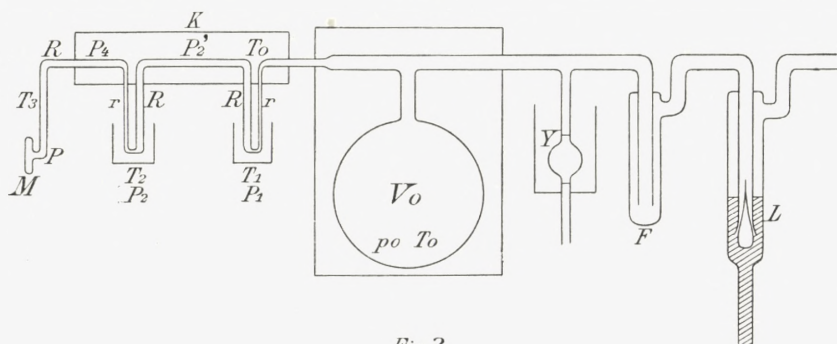


Fig 2

manometer is connected with a large glass vessel the volume of which has been measured to be V_0 . The widest tubes

¹ Martin Knudsen: Det Kgl. Danske Videnskabernes Selskab. Matematisk-fysiske Meddelelser VII, 15, 1927.

in the system have a radius of abt. 1 mm. The two pieces of tubing marked R in the figure have equal radii:

$$R = 0.099655 \text{ cm.}$$

and the two pieces of tubing marked r have equal radii, viz.

$$r = 0.026845 \text{ cm.}$$

These four pieces of tubing were as circularly cylindrical as they could be found in a large collection of tubes. Their upper joints, which during the experiments should have the same temperature, were surrounded by a rather large water bath, K , contained in a rectangular copper box. The vessel with the volume V_0 , abt. 1.2 litres, was likewise placed in a water bath the walls of which were well insulating for heat. Y is a pipette, the gauge vessel, placed in a water bath. It may be filled with and emptied of mercury through the tube at the bottom, and it serves to calibrate the hot-wire manometer, its volume between the marks being measured to 8.8746 cm^3 . F is a trap which is kept in liquid air during the experiments, and L is a mercury seal with a ground glass float which can shut off the apparatus from the pipette system serving to introduce a gas of known pressure into the apparatus. The glass float very effectually prevents the penetration of mercury vapours into the apparatus, and the tube below the small gauge vessel is very narrow, so that by this way too the entrance of mercury vapours will be negligible.

During the first measurement on the potentiometer the two joints between the tubes R and r are placed each in a separate bath, the temperatures of which are measured or known. Thereupon the two baths are interchanged and a second measurement is made. From the two measurements the ratio between the two pressures may be found.

Let fig. 3 be a circularly cylindrical tube closed at both ends. Let the radius of the tube be r and let one end of it have the absolute temperature T_1 , the other T_2 . In the



Fig 3

state of equilibrium the pressures of the gas contained in the tube will be different at the two ends. If they be designated p_1

and p_2 , as indicated in the figure, $p_1 - p_2$, i. e. the quantity which I term the thermal molecular pressure will differ from 0 when $T_1 - T_2$ does so.

We may know beforehand that the thermal molecular pressure must be a very complicated function of the temperature, the pressure, and the radius of the tube, therefore I have considered it advisable to make a series of measurements at such small temperature differences that $p_1 - p_2$ may with sufficient approximation be put proportional to $T_1 - T_2$ at all pressures. Hence for the tube with the radius r we put $p_1 - p_2 = f(T_1 - T_2)$, and for the tube with the radius R we put $p_1 - p_2 = F(T_1 - T_2)$, on the assumption that the mean pressures in the two tubes may with approximation be put equal.

With the designations of pressures and temperatures given in fig. 2 we may then note the following set of equations:

$$P_1 - p_0 = f(T_1 - T_0)$$

$$P_2 - P_1 = F(T_0 - T_1)$$

$$P_2 - P_2' = F(T_2 - T_0)$$

$$P_4 - P_2 = f(T_0 - T_2)$$

$$P - P_4 = F(T_3 - T_0)$$

If now we interchange the two baths whose temperatures were designated T_1 and T_2 , the pressures will change

throughout except in the large vessel V_0 , for compared to its volume the rest of the volumes are negligible. If the new pressures are designated p with the same indices which P had before, we shall get the following set of equations:

$$p_1 - p_0 = f(T_2 - T_0)$$

$$p'_2 - p_1 = F(T_0 - T_2)$$

$$p_2 - p'_2 = F(T_1 - T_0)$$

$$p_4 - p_2 = f(T_0 - T_1)$$

$$p - p_4 = F(T_3 - T_0)$$

If the two sets of equations are added separately, we get:

$$P - p_0 = F(T_2 - T_1) + f(T_1 - T_2) + F(T_3 - T_0)$$

$$p - p_0 = F(T_1 - T_2) + f(T_2 - T_1) + F(T_3 - T_0),$$

from which by subtraction

$$\frac{1}{2}(P - p) = (f - F)(T_1 - T_2)$$

and hence, $\frac{1}{2}(P - p)$ being designated by Δp and $T_1 - T_2$ by ΔT ,

$$f - F = \frac{\Delta p}{\Delta T}.$$

The quantity f may be characterised as being equal to $\frac{dp}{dT}$ in the tube with the radius r , while F is equal to $\frac{dp}{dT}$ in the tube with radius R , in which the pressure is very nearly equal to that in the first-mentioned tube.

In the series of experiments in question in which F and f were determined, the temperatures ($T_0 - 273^\circ$) of the water baths were kept at 20° centigrade. T_1 was kept at the temperature of melting ice, the bath consisting of scraped ice in a Dewar vessel. T_2 was kept 40° higher by a water bath which was continually stirred by a current

of air, while the loss of heat to the surroundings was compensated by electric heating. The temperature of this bath was read on a mercury thermometer graded $\frac{1}{10}$ and bent in an angle so that it could be placed under the copper box *K*. The two baths were both placed on a revolving stand, so that they could be easily and quickly interchanged.

The temperature of the manometer was throughout that of melting ice, but as will be seen, neither this temperature nor T_0 , that of the water baths, enters into the equation by which $f-F$ is determined. Besides this the method further presents the advantage that the volumes changing temperatures are not altered by the interchange, and thus changes in pressure caused by Gay-Lussac's expansion are avoided. Finally, what is most essential is that the areas of the glass surfaces subjected to the changes in temperature is here reduced to a minimum of abt. 8 cm². For it is only in the comparatively narrow and short pieces of tubing that the temperature changes cause the harmful adsorption phenomena.

Example of a Measurement.

All measurements were, in all essentials, made in the same manner, so we shall here only describe one chosen at random from the entire material.

The whole apparatus with pipette system and mercury manometer was exhausted by means of a mercury diffusion pump. Between this and the apparatus was inserted a trap cooled in liquid air. When after pumping for a short time the apparatus was almost devoid of air, electric heating coils were placed round each of the bends of the tubes under the copper box. Thus these tubes were baked out,

being kept heated to a temperature of abt. 330° centigrade for 10—12 hours while the pump was at work now and then. This heating was intended to diminish the harmful adsorption effects, and was to some extent successful, though unfortunately not absolutely. The tubes used were of good Thüring glass, an experiment with Geräte glass and Pyrex glass having shown that these kinds did not present such advantages that it would be profitable to use them.

When the heating was finished and also the exhaustion, the result of which was followed on the hot wire manometer and in some cases on an absolute manometer, hydrogen was brought into the apparatus. This hydrogen was taken from a steel receptacle and had been tested and proved sufficiently pure. It was dried by passing through a trap cooled in liquid air. Its influx could be so accurately regulated that the desired pressure in the mercury manometer could be produced with great approximation. In the experiment to be described here the reading on the mercury manometer was 21.514 cm. mercury pressure at 20° . By means of the pipette system a fraction hereof was introduced into the apparatus, liquid air being placed round the trap *F* (fig. 2). From the known volumes of the pipette system and the apparatus the pressure in the apparatus was found to be 718.6 bar. The mercury seal *L* (fig. 2) was closed, and a water bath of 20° centigrade placed round both bends of the tubes, *r* and *R*.

The resistance of the manometer wire was 743.3 ohms at 0° . Wheatstone's bridge was adjusted so that there would be no current in its galvanometer when the wire was heated so much that its resistance would be 900 ohms. The mean temperature of the wire is then abt. 60° centi-

grade. The potentiometer whose total resistance was 11000 ohms was shunted with a resistance of 310 ohms in order to obtain a suitably large reading (between 9000 and 10000 ohms). This is of importance for the interpolation which is made by measuring the deflection of the galvanometer mirror caused by a change of 1 ohm in the potentiometer.

The table below shows a column indicating the hour when the measurements were made. The next two columns show the temperatures t_1 and t_2 in degrees centigrade of the baths surrounding the bends of the tubes, and under Comp., finally, are given the readings on the potentiometer.

Time	t_1	t_2	Comp.
11 ^h 45	20°	20°	9656,97
57	40°,63	0°	9745,47
12 ^h 10	0°	40°,40	9568,88
23	40°,58	0°	9745,10
35	20°	20°	9656,32
47	0°	40°,54	9568,60
59	40°,40	0°	9744,32
1 ^h 11	0°	40°,20	9568,92
24	20°	20°	9655,14

From this series it will be seen that the measurements were made at very nearly equal intervals of time. This was done on account of the adsorption effects. Between the measurements are interposed some with both bends of the tubes at the same temperature 20° so as to follow the slow changes of pressure in the apparatus. It was as far as possible attempted to do away with these by grouping

the measurements three and three together as shown in the table.

By taking means the table is reduced to the following two

t_1	t_2	Comp.	$\Delta \text{Comp.} =$ $\text{Comp.}_{t_1, t_2} - \text{Comp.}_{20, 20}$	$\frac{\Delta \text{Comp.}}{t_1 - t_2}$	Mean values $\frac{\Delta \text{Comp.}}{t_1 - t_2}$
20°	20°	9656,65			
40°,61	0°	9745,29	+ 88,64	2,1827	2,1776
0°	40°,40	9568,88	- 87,77	2,1725	
20°	20°	9655,73			
40°,40	0°	9744,32	+ 88,59	2,1928	2,1736
0°	40°,37	9568,76	- 86,97	2,1543	

The two measurements made independently of each other, and which were almost independent of the measurements at 20°, 20°, have thus given the following values for $\frac{\Delta \text{Comp.}}{t_1 - t_2}$, 2.1776 and 2.1736, hence the mean value, $t_1 - t_2$ being designated by ΔT .

$$\frac{\Delta \text{Comp.}}{\Delta T} = 2.1756 = \text{Measurement.}$$

In connection with these measurements gaugings were made, as a rule two, one before and the other after the measurements at different temperatures had been made. During the gauging measurements the bends of the tubes were kept at the same temperature abt. 20°, both bends being placed in a single large water bath. In connection with the above-mentioned measurements the following gauge-measurements were made, partly with the gauge vessel *Y* empty (fig. 2) partly when it was filled with mercury

	Comp.	Comp. (empty-full)	Mean <i>d</i> Comp.
Y empty	9655,14		
Y full	9622,79	32,28	
Y empty	9655,00		
			32,30 = gauge
Y empty	9650,49		
Y full	9618,04	32,32	
Y empty	9650,22		

The compensation change thus produced, viz. d Comp. = 32.30 = gauge is due to the fact that the volume $V = 1219.04 + 8.8746 \text{ cm}^3$ of the gas content of the whole apparatus has been diminished by the volume $\Delta v = 8.8746 \text{ cm}^3$ of the gauge vessel. This reduction of the volume produces an increase of the pressure dp which, when the pressure in the apparatus is designated p , is determined by

$$\frac{dp}{p} = \frac{8.8746}{1219.04} = 0.007280.$$

Since here, where the relative changes are small, we can put the changes in pressure proportional to the changes in compensation we get

$$\frac{\Delta p}{dp} = \frac{\Delta \text{Comp.}}{d \text{Comp.}} = \Delta T \cdot \frac{\text{measurement}}{\text{gauge}}$$

and consequently

$$10^4 \frac{\Delta p}{p \Delta T} = 72,80 \cdot \frac{\text{measurement}}{\text{gauge}}.$$

In the example here considered, where measurement = 2.1756 and gauge = 32.30 we thus get

$$10^4 \frac{\Delta p}{p \Delta T} = 4.904.$$

Such a determination was made at eleven different pressures p , which very nearly formed a geometrical progression, 19082 bar being the highest pressure and 27.15 the lowest, while the quotient was equal to the square root of the ratio between the radii of the two tubes used in the apparatus. Judging from repetitions following immediately after one another the uncertainty of the values found only amounts to a few per mille, but as we shall see later, the real uncertainty is much greater, especially at low pressures.

Results of the Measurements and their provisional Treatment.

The measurements made with the temperatures 0 and 40 degrees centigrade at various pressures p' gave the following values for $10^4 \frac{\Delta p'}{p' \Delta T}$

number $n =$	0	1	2	3	4	5
p' Bar	= 19082	9920	5142	2705	1388,9	718,6
$10^4 \frac{\Delta p'}{p' \Delta T}$	= 0,0790	0,2528	0,7456	1,648	3,314	4,904
number $n =$	6	7	8	9	10	
p' Bar	= 373,5	193,2	100,76	52,22	27,15	
$10^4 \frac{\Delta p'}{p' \Delta T}$	= 5,424	4,719	3,481	2,542	1,786	

The measured values of p' agree very closely with the pressures calculated from the formula $p = p_0 \left(\frac{r}{R}\right)^{\frac{n}{2}}$ so that interpolations may be made with great certainty which give $10^4 \frac{\Delta p}{p \Delta T}$ for the pressures p given in the geometrical progression. The interpolated values are given in the following table, together with some other quantities to be mentioned later on.

$\frac{p}{\text{Bar}}$	$10^4 \frac{\Delta p}{p \Delta T}$	$10^4 \frac{f}{p}$	$\frac{1}{u} = \frac{2 T f}{p}$
19082	0,0790	0,0857	0,00502
9904	0,2537	0,2774	0,01626
5140	0,7464	0,8321	0,04878
2668	1,678	1,955	0,1146
1385	3,323	4,155	0,2436
718,7	4,904	6,859	0,4021
373,0	5,422	9,577	0,5614
193,6	4,724	11,583	0,6790
100,5	3,474	13,051	0,7650
52,15	2,542	14,125	0,8280
27,07	1,782	14,833	0,8695

For the further treatment of the observation series we remind the reader that for a tube with radius r , in which there is the pressure gradient dp originating from the temperature gradient dT , we have put $\frac{dp}{dT} = f$, while for the wide tube with radius R we put $\frac{dp}{dT} = F$.

Further it was proved that

$$f - F = \frac{\Delta p}{\Delta T}$$

or

$$10^4 \frac{f}{p} - 10^4 \frac{F}{p} = 10^4 \frac{\Delta p}{p \Delta T}$$

where Δp and ΔT are just the quantities that with the same designation enter into the tabulated values for $10^4 \frac{\Delta p}{p \Delta T}$. Hence we may consider $f - F$ as the quantity observed at different pressures. Our problem is now to find both f and F from the differences observed, which may be done by theoretical considerations that have been found tenable by previous experiments.

For a tube with the radius r I have previously¹ found an expression for f or $\frac{dp}{dT}$, which by inserting the constants gives

$$f = \frac{0,02996}{r + 0,01191 r^2 p}.$$

If r in this expression be replaced by R , we get F , and from the values thus found we calculate $10^4 \frac{f}{p}$ and $10^4 \frac{F}{p}$ and from these again $10^4 \frac{f}{p} - 10^4 \frac{F}{p}$, which is a provisionally found value for $10^4 \frac{\Delta p}{p \Delta T}$. If we compare the values of $10^4 \frac{\Delta p}{p \Delta T}$ thus calculated with those observed, we find, in the case of the three greatest pressures, deviations not amounting to more than 5 p. c. of the values. For a pressure of 19082 bar $10^4 \frac{F}{p}$ is calculated to be 0.0067 and for a pressure of 9904 bar $10^4 \frac{F}{p}$ is calculated to be 0.0237. Having $10^4 \frac{f}{p} - 10^4 \frac{F}{p} = 10^4 \frac{\Delta p}{p \Delta T}$ we find by adding the calculated values for $10^4 \frac{F}{p}$ to those observed for $10^4 \frac{\Delta p}{p \Delta T}$ that for the pressures

$$19082 \text{ bar we get } 10^4 \frac{f}{p} = 0.0857$$

and for

$$9904 \text{ bar we get } 10^4 \frac{f}{p} = 0.2774.$$

These values have been tabulated and are employed to calculate the rest of the values given for $10^4 \frac{f}{p}$.

In this calculation we avail ourselves of the fact that $\frac{f}{p}$ at the pressure 19082 is equal to $\frac{F}{p}$ at the pressure $19082 \cdot \frac{r}{R}$, that is to say, at the pressure 5140, for which we have an observation of $10^4 \frac{f}{p} - 10^4 \frac{F}{p}$. Hence to this

¹ Martin Knudsen, Ann. d. Phys. Bd. 33, p. 1444, 1910.

observation, the tabulated 0.7464, we need only add 0.0857 to find $10^4 \frac{f}{p}$ valid for the pressure 5140. This proceeding is continued throughout the table so that for each pressure we have the corresponding value for $10^4 \frac{f}{p}$. In view of the following calculations and considerations the next column in the table is formed, $\frac{1}{u} = 2 T \cdot \frac{f}{p}$ where T is the mean temperature 293.1° at which the measurements were made. The quantities $\frac{1}{u}$ thus calculated indicate how great is the effect of the thermal molecular pressure in a tube of the given radius r .

The formula $f = \frac{0,02996}{r + 0,01191 r^2 p}$ warrants this proceeding in the case of the large pressures. Hence for a tube with radius r and pressure p and another with radius R and pressure P we have $\frac{f}{p} = \frac{0,02996}{rp + 0,01191 (rp)^2}$ and $\frac{F}{P} = \frac{0,02996}{RP + 0,01191 (RP)^2}$. From this we see that $\frac{f}{p} = \frac{F}{P}$ when $rp = RP$ which was just what was made use of in the calculation.

That this proceeding holds good for all pressures may be seen by the following consideration. We will take it for granted that when a closed circularly cylindrical tube, containing a gas at the pressure p , has different temperatures at the two ends, the difference in pressure found between the two ends in the state of equilibrium will be independent of the way in which the temperature varies from end to end. From this it follows that when an increase of temperature dT is found on the length dl of the tube, this will involve an increase of pressure dp , which is independent of dl , but determined by other quantities. What these are may be determined by considering the

quantity $\frac{dp}{dT}$. This quantity is dependent both on the dimensions of the tube and on the physical properties of the gas. Since the dimensions of the tube only comprise its length and radius and since the length, as we just stated, does not influence $\frac{dp}{dT}$, the radius r will be the only dimension of the tube of which $\frac{dp}{dT}$ may be a function.

Hence we may put $\frac{dp}{dT} = \Phi \left(r, \frac{p}{T} \right)$ (r , the physical properties of the gas). Since $\frac{p}{T}$ is a pure number the physical properties of the gas that can be taken into account can only be a length L which enters into the equation so that we

can put $\frac{dp}{dT} = \Phi \left(\frac{r}{L} \right)$ or $2 T \frac{f}{p} = 2 \Phi \left(\frac{r}{L} \right)$. If we have a

series of tubes of different radii and assume that they all of them have the same temperature and all contain hydrogen, their hydrogen content will be determined entirely by the dimensions of the tubes and the mean free path λ of the hydrogen. The quantity L in the above-mentioned formula may therefore be put identical with λ . If now we remember that we have $p \lambda = \lambda_1$, we get $\frac{r}{L} = \frac{rp}{\lambda_1}$ and hence

$$\frac{f}{p} = \frac{1}{T} \Phi \left(\frac{rp}{\lambda_1} \right).$$

Here λ_1 is the mean free path of the hydrogen at the pressure 1 bar and the temperature T , that is to say, independent of r and p , so the expression shows that when

r and p vary in such a way that their product is kept constant $\frac{f}{p}$ will remain unaltered at constant temperature. As has been mentioned, the calculations made have been based on this rule, and it is important in giving expressions for the thermal molecular pressure to keep to the formula

$$\frac{dp}{dT} = \frac{p}{T} \Phi\left(\frac{r}{\lambda}\right).$$

The tabulated quantity $\frac{1}{u} = 2T \frac{f}{p} = 2T \frac{1}{p} \frac{dp}{dT}$ is thus a function of $\frac{r}{\lambda}$ alone, and our next problem will be to find an expression for this functional dependency. For the solution of this problem it must be remembered that the values found in the table for $\frac{1}{u}$ were calculated successively, so that any inaccuracy in one of the measurements at high pressures will make its influence felt at all the lower pressures. For these, therefore, all the errors will be added up. This unfortunate circumstance may, however, be entirely avoided, as will be shown in the following.

Theoretical Considerations in the Formation of a Formula for the Thermal Molecular Pressure.

Reynolds' formula, which was given in the introduction, may be arrived at by the following simple kinetic consideration. Let N be the number of gas molecules in each cm.^3 , m the mass of each molecule, and c the molecular velocity. \bar{c} denotes the mean value of the molecular velocities, and \bar{c}^2 the mean value of the squares of the velocities. n denotes the number of impacts that is to say, the number of molecules which in each second passes through a cm.^2 coming from one side of it. If the pressure of the gas be p , its absolute temperature T , and its molecular

weight M , the kinetic theory in conjunction with the simple equation of state will give the following fundamental expressions

$$p = \frac{1}{3} Nm \bar{c}^2 \quad \text{and} \quad n = \frac{1}{4} N \bar{c}$$

and it follows from Maxwell's law of the distribution of velocities that

$$\frac{1}{3} \bar{c}^2 = \frac{\pi}{8} (\bar{c})^2 \quad \bar{c} = 14550 \sqrt{\frac{T}{M}}$$

If we can disregard the effect of the mutual impacts of the molecules in the places where the temperature varies from place to place, we have, when the state is to be a state of equilibrium, that the number of impacts n must have the same value everywhere. For let us suppose that the two vessels have the absolute temperatures T_1 and T_2 , and that the total temperature difference $T_1 - T_2$ is found in a single definite cross-section of the communication tube. Then, for the molecules coming from one side towards this cross-section we have the number of impacts $n_1 = \frac{1}{4} N_1 \bar{c}_1$ and for those coming from the other side we have $n_2 = \frac{1}{4} N_2 \bar{c}_2$. As it is presupposed that no more molecules pass through the cross-section in one direction than in the opposite direction, we must have $n_1 = n_2$ and hence $N_1 \bar{c}_1 = N_2 \bar{c}_2$. From the fundamental equation we see that $\frac{p_1}{p_2} = \frac{N_1 \bar{c}_1^2}{N_2 \bar{c}_2^2} = \frac{N_1 (\bar{c}_1)^2}{N_2 (\bar{c}_2)^2}$ and consequently $\frac{p_1}{p_2} = \frac{\bar{c}_1}{\bar{c}_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}}$. If the difference in temperature $T_1 - T_2$ is infinitely small and equal to dT , we get the expression

$$\frac{dp}{p} = \frac{1}{2} \frac{dT}{T} \quad \text{or} \quad \frac{dp}{dT} = \frac{p}{T} \cdot \frac{1}{2}$$

This expression can, however, only be expected to be valid when we can disregard the number of the mutual impacts of the molecules as compared with the number of impacts against the walls of the tubes, or, in other words, when the cross-section dimensions of the tube are negligible compared with the mean free path λ of the gas molecules. If this requirement is not satisfied, $\frac{dp}{p}$ may be expected to be less than $\frac{1}{2} \frac{dT}{T}$, and for a cylindrical tube with radius r it may be expected that $\frac{dp}{p}$ will decrease when the ratio $\frac{2r}{\lambda}$ increases. For the case when $\frac{2r}{\lambda}$ is small compared with 1, I have previously¹ given the following condition of equilibrium

$$\frac{dp}{p} = \frac{1}{1 + \frac{2r}{\lambda}} \frac{d\bar{c}}{\bar{c}}.$$

Since $\frac{d\bar{c}}{\bar{c}} = \frac{dT}{2T}$ the expression is transformed into

$$\frac{dp}{p} = \frac{1}{1 + 2\frac{r}{\lambda}} \frac{dT}{2T}.$$

For the correctness of this expression I have previously, *l. c.*, endeavoured to give reasons. These do not now seem to me to be conclusive. Hence I will for the time being substitute an unknown factor for the factor 2 in the denominator.

In all cases in which r is not negligible compared with λ there will be currents in the tube in the state of equilibrium. A current along the wall of the tube from the cold to the warm end will cause the pressure at the warm end to be greater than that at the cold end, and

¹ Martin Knudsen, *Ann. d. Phys. Bd. 31*, p. 223, 1910.

this gradient of pressure will cause a current to flow along the axis of the tube from the warm to the cold end.

For the momentum M received by each surface unit of the tube owing to the molecular velocity \bar{c} varying through the tube, I have previously¹ given an expression which with a slight transcription gives

$$M = -\frac{3\pi}{128} p \varrho_1 \bar{c} \lambda \frac{d\bar{c}}{dl} k_1$$

where ϱ_1 denotes the density of the gas at a pressure of 1 bar and the temperature T , while dl denotes an element of the length of the tube. k_1 is a quantity which for very small values of $\frac{r}{\lambda}$ may be put equal to 1 and increases with increasing values of $\frac{r}{\lambda}$ to a limit which according to previous measurements lies between 2 and 3.

Since

$$\bar{c} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{1}{\varrho_1}} \quad \text{and} \quad \frac{d\bar{c}}{c} = \frac{dT}{2T} \quad \text{we get} \quad M = -\frac{3}{32} p \lambda \frac{1}{T} \frac{dT}{dl} \cdot k_1.$$

For the momentum B received by each surface unit in each second when the pressure gradient $\frac{dp}{dl}$ produces a current at constant temperature, calculation and experiments give

$$B = \frac{3 \cdot 0,81}{32} \sqrt{\frac{\pi}{8}} \sqrt{\frac{\varrho_1}{\eta}} r^2 p \frac{dp}{dl}$$

where η denotes the coefficient of viscosity which is connected with λ by the equation

$$\lambda = \frac{1}{0,49} \sqrt{\frac{\pi}{8}} \frac{\eta}{p \sqrt{\varrho_1}} \quad \text{so that} \quad B = \frac{3\pi}{256} \frac{0,81}{0,49} \frac{r^2}{\lambda} \frac{dp}{dl}.$$

¹ Martin Knudsen, Ann. d. Phys. Bd. 31, p. 214, 1910.

If temperature gradient and current are found at the same time, each length unit of the tube will receive the momentum $2\pi r(M+B)$ so that the condition of equilibrium will be $2\pi r(M+B) + \pi r^2 \frac{dp}{dl} = 0$. Hence, by the insertion of M and B we get

$$\frac{dp}{dT} = \frac{1}{\frac{8}{3} \frac{1}{k_1} \frac{r}{\lambda} + \frac{\pi}{16} \frac{0,81}{0,49} \frac{1}{k_1} \frac{r^2}{\lambda^2}} \cdot \frac{p}{2T}.$$

By a previous¹ series of experiments I have shown that this expression may be assumed to be correct when $\frac{r}{\lambda}$ is large.

An expression of this form and the expression given for small values of $\frac{r}{\lambda}$ may be embodied in the following

$$\frac{dp}{dT} = \frac{1}{\left(1 + a' \frac{r}{\lambda}\right)^2} \frac{p}{2T}$$

and it may then be expected that a' for small values of $\frac{r}{\lambda}$ will be of the same order of size as 1. For if we put $a' = 1$, the expression will be identical with the above-mentioned

$$\frac{dp}{dT} = \frac{1}{1 + 2 \frac{r}{\lambda}} \frac{p}{2T}.$$

If we compare the equation containing a' with that into which k_1 enters, we should expect a' to decrease with increasing values of $\frac{r}{\lambda}$. The following expression satisfies this requirement

$$a' = a \frac{1 + b \frac{r}{\lambda}}{1 + c \frac{r}{\lambda}} \quad \text{where } b < c.$$

¹ Martin Knudsen, Ann. d. Phys. Bd. 33, p. 1435, 1910.

If we insert this value for a' , we get the following general formula for the thermal molecular pressure

$$\frac{dp}{dT} = \frac{1}{\left(1 + a \frac{r}{\lambda} \frac{1 + b \frac{r}{\lambda}}{1 + c \frac{r}{\lambda}}\right)^2} \frac{p}{2T}. \quad (1)$$

The mean free path λ is, however, a function of p and T . We have $\lambda p = \lambda_1$ where λ_1 is the mean free path at a pressure of 1 bar and the temperature T . For the temperature interval at which my measurements were made the temperature dependency of the viscosity of hydrogen is given by the formula

$$\eta = \eta_0 \left(\frac{T}{273}\right)^{0,682}$$

and since

$$\lambda p = \frac{1}{0,49} \sqrt{\frac{\pi}{8}} \frac{\eta}{\sqrt{\varrho_1}} = \frac{1}{0,49} \sqrt{\frac{\pi}{8}} \frac{\eta}{\sqrt{\varrho_0}} \left(\frac{T}{273}\right)^{\frac{1}{2}}$$

where ϱ_0 is the density of the hydrogen at the pressure 1 bar and the temperature of melting ice ($T = 273^\circ$), we get

$$\frac{1}{\lambda} = \frac{p}{\frac{1}{0,49} \sqrt{\frac{\pi}{8}} \frac{\eta_0}{\sqrt{\varrho_0}} \left(\frac{T}{273}\right)^{1,182}}.$$

Putting for hydrogen

$$\frac{\eta_0}{\sqrt{\varrho_0}} = 8,933$$

we get

$$\frac{1}{\lambda} = 0,08753 p \left(\frac{273}{T}\right)^{1,182}. \quad (2)$$

Determination of the Constants in the General Formula for the Thermal Molecular Pressure.

Having tried various formulas I have chosen the one given above as that which with the fewest constants agrees

best with the experimental material at the mean temperature 20.1° centigrade. If we remember that, when describing the results of our measurements, we put

$$2 T \frac{f}{p} = 2 T \frac{dp}{p dT} = \frac{1}{u}$$

we should according to formula (1) be able to put

$$\frac{dp}{dT} = \frac{1}{u} \cdot \frac{p}{2T}, \text{ where } u = \left(1 + a \frac{r}{\lambda} \frac{1 + b \frac{r}{\lambda}}{1 + c \frac{r}{\lambda}} \right)^2$$

and
$$\frac{r}{\lambda} = 0,08753 \cdot p \cdot r \left(\frac{273}{T} \right)^{1,182}.$$

By formation of differences in the table containing $\frac{1}{u}$ as a function of p and thence of $\frac{r}{\lambda}$ were found the following provisional values for the constants $a = 2.212$, $b = 2.85$, $c = 20.0$. These constants which must be expected to be influenced by the errors due to summation and to the use of earlier and uncertain observations, must now be improved, these sources of error being avoided. This is done by returning to the directly observed values $10^4 \frac{\Delta p}{p \Delta T}$ given in the table. From this series a new series is formed by multiplication with $10^{-4} \cdot 2T$, where T is the mean temperature 293.1° . In this way we get a value for $2 T \frac{\Delta p}{p \Delta T}$ which is regarded as the quantity observed at each single pressure.

Forming U from u by replacing r by R we get

$$2 T \frac{\Delta p}{p \Delta T} = \frac{1}{u} = \frac{1}{U}$$

that is to say, an equation for each of the observations of the table. From these equations a , b and c are determined by the method of least squares, and thus we find

$$a = 2.46 \quad b = 3.15 \quad c = 24.6.$$

In this calculation it is supposed that all the measurements of $2T \frac{\Delta p}{p \Delta T}$ have been made with equal accuracy, so that occurring systematical errors will influence the constants.

Hence the result of the investigation is that the thermal molecular pressure in a circularly cylindrical tube with the radius r may be expressed as follows

$$\frac{dp}{dT} = \frac{1}{\left(1 + 2,46 \frac{r}{\lambda} \cdot \frac{1 + 3,15 \frac{r}{\lambda}}{1 + 24,6 \frac{r}{\lambda}}\right)^2} \cdot \frac{p}{2T}$$

when putting for hydrogen

$$\frac{1}{\lambda} = 0,08753 p \left(\frac{273}{T}\right)^{1,182}.$$

In the case of such great temperature differences that the differential formula cannot be directly applied, an integration may be undertaken, the last equation giving

$$\frac{dp}{p} = \frac{1,182}{T} dT - \frac{d\lambda}{\lambda}$$

which, inserted in the last but one, gives

$$\frac{dT}{2T} = \frac{d\lambda}{\lambda} \frac{1}{2,364 - \frac{1}{u}}.$$

If in this we insert the value found for u the result will be an equation which can easily be integrated. Such an

integration between the limits $293^{\circ} \pm 20^{\circ}$ showed that we are entirely warranted in applying the differential formula without integration within these limits.

In order to investigate how the experimental results are rendered by the differential formula with the constants found the following table was calculated.

p Bar	$\frac{r}{\lambda}$ at 20° C.	$2 T \frac{\Delta p}{p \Delta T}$		observed— calculated
		observed	calculated	
19082	41,22	0,00463	0,00464	— 0,00001
9904	21,39	0,01486	0,01486	0,00000
5140	11,103	0,0437	0,0425	+ 0,0012
2668	5,763	0,0986	0,1024	— 0,0038
1385	2,991	0,195	0,196	— 0,001
718,7	1,552	0,287	0,285	+ 0,002
373,0	0,8057	0,318	0,317	+ 0,001
193,6	0,4182	0,276	0,278	— 0,002
100,5	0,2170	0,204	0,207	— 0,003
52,15	0,1126	0,149	0,146	+ 0,003
27,07	0,0585	0,105	0,107	— 0,002

From the above table it will be seen that the general formula gives a very good representation of the experimental results within the range investigated. The differences between the observed and the calculated values is of the order of 1 p. c. of the observed values except for the observation made at the pressure of 2668 bar, where the difference amounts to almost 4 p. c. This may possibly be due to an incorrect determination of the pressure which is confirmed by the following.

As it would be of interest to investigate other temperatures, two other series of experiments were made, simul-

taneously with those between 0° and 40° , at the same pressures. In one of these the one bath was scraped ice, the other a mixture of carbonic acid and ether. The temperature of this mixture was put at -78.5°C . In the second series of experiments liquid air was used in one bath, while the other was again a mixture of carbonic acid and ether. The temperature of the liquid air was determined by means of the usual small floats. In these two series of measurements the quantity $2T \frac{\Delta p}{p \Delta T}$ given in the following tables was again determined. For comparison with the general formula $\frac{1}{u} - \frac{1}{U}$ was calculated by integration and the result subtracted from the observed values for $2T \frac{\Delta p}{p \Delta T}$. The mean temperature T (absolute) of the baths used is also given in the tables, as well as the values $\frac{r}{\lambda}$ calculated from p and T .

p	$T = 233.75^\circ$ Ice and Carbonic Acid			$T = 138.3^\circ$ Carbonic Acid and Liquid Air		
	$\frac{r}{\lambda}$	$2T \frac{\Delta p}{p \Delta T}$	observed— calculated	$\frac{r}{\lambda}$	$2T \frac{\Delta p}{p \Delta T}$	observed— calculated
19082	53,87	0,0031	+ 0,0003	100,18	0,0010	+ 0,0002
9920	28,00	0,0093	0,0000	52,08	0,0031	+ 0,0001
5142	14,52	0,0288	+ 0,0007	27,00	0,0098	- 0,0001
2705	7,636	0,067	- 0,005	14,20	0,025	- 0,003
1389	3,921	0,153	- 0,001	7,292	0,071	- 0,004
718,6	2,029	0,255	+ 0,004	3,773	0,151	- 0,007
373,5	1,054	0,313	+ 0,004	1,961	0,254	+ 0,001
193,2	0,5454	0,293	+ 0,001	1,014	0,301	0,000
100,8	0,2844	0,227	- 0,001	0,529	0,274	- 0,002
52,22	0,1474	0,170	+ 0,009	0,274	0,217	- 0,005
27,15	0,0766	0,117	+ 0,001	0,143	0,157	+ 0,008

The differences between the observed and the calculated values are not any greater than might reasonably be expected. A systematic course in the differences only appears in the series with carbonic acid and liquid air and is not marked enough to give reasons for a change of the constants in the general formula. The greatest percentage difference between the observed and the calculated values appears in both series at a pressure of 2705 bar, that is to say, at the same pressure at which the greatest deviation in the series 40°-ice was found. This would seem to indicate that an error has crept in in the determination of the pressure, which is not, however, so great that we should feel justified in leaving the observations at this pressure out of consideration.

In order to investigate the thermal molecular pressure at higher temperatures a series of experiments were conducted at a mean temperature of abt. 260°. The values observed for $2T \frac{\Delta p}{p \Delta T}$ here proved to be abt. 10 p. c. lower than those calculated by the formula given above. For pressures higher than 1000 bar this discrepancy is chiefly due to the fact that the temperature dependency given in the formula $\eta = \eta_0 \left(\frac{T}{273} \right)^{0.682}$ is not valid at high temperatures. Breitenbach's¹ exponent 0.5832 instead of 0.682 would give a considerably better correspondence. At lower pressures such an alteration of the exponent will not, however, greatly alter the calculated values, and the explanation may be perhaps that the harmful adsorption phenomena make their influence more felt at high than at low temperatures because the adsorption processes take place more rapidly in the first case.

¹ Breitenbach, Ann. d. Phys. Bd. 67, 1899, p. 817.

In the above I have mentioned that as a guide in the formation of the general empirical differential formula I used the theoretical expression

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

which I thought must hold good when r is very small but not negligible compared with λ . For this case the empirical formula gives

$$\frac{dp}{dT} = \frac{1}{1 + 2a\frac{r}{\lambda}} \frac{p}{2T}.$$

If the theoretical formula were correct, the measurements should thus have given $a = 1$. They have, however, given $a = 2.46$, which is a considerable discrepancy. Whether this is due to an incorrect determination of the quantity a on account of adsorption phenomena or whether some error attaches to the theoretical formula I dare not say.

In order to elucidate this latter question, a theoretical derivation of the formula ought to be made, based solely on the kinetic theory of gases. Such a derivation would presumably be very difficult in the general case, but would seem feasible here where we are considering the case of r being small compared with λ . In case this calculation were made and in case it would in future be possible to avoid the adsorption phenomena so that a could be determined with sufficient accuracy, this method presents a direct measurement of λ , this quantity, the mean free path, of which it is now hardly possible to give an exact definition, would in that case be directly compared with the radius r of the tube, and we should have another

means of obtaining information of the direction in which the molecules moved after the so-called mutual impacts.

With regard to the influence of the adsorption the following remark may be made. In the way the apparatus was arranged we can hardly suppose that it contained mercury in other places than in the trap which was cooled in liquid air. It may be supposed, however, that there will be adsorbed water all over the walls of the glass, which will pass at an extremely slow rate towards the trap with liquid air. This passage will presumably be so slow and regular when the temperature of the apparatus is kept constant that the hydrogen pressure will practically be the same throughout. Otherwise when the joint of a tube is heated or cooled. In the former case water is liberated from the walls, in the latter case water is adsorbed. Both processes will produce currents which are different in the wide tube from those in the narrow tube, and these currents may be expected to produce differences in pressure which will become sources of error in the measurements.

Finally, it cannot be precluded that the hydrogen itself may to some extent be adsorbed to the glass wall. Even if such an adsorption is not appreciably altered at the small differences of temperature employed in the experiments, it will, however, cause λ to be smaller close to the wall of the tube than it is at the axis of the tube, and thus explain that the constant a has been found greater than 1.

It might perhaps be supposed that the harmful effect of the adsorption phenomena would appear less at high than at low temperatures. My measurements do not indicate this, however. The adsorption phenomena cause currents

in the tubes lasting at least twenty-four hours and probably several days and nights, so that a stationary condition is not obtained within a reasonable time. Hence it is a reasonable supposition that even if the adsorbed masses are much smaller at high than at low temperatures, the liberation of adsorbed substance at increased temperature will take place at a much quicker rate with a high than with a low temperature, and produce just as strong or perhaps stronger currents in the tubes.

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MATHEMATISK-FYSISKE MEDDELELSER

UDGIVNE AF

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