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Absolute measurement of mercury vapour pressure at temperatures from 7° to 25° C, and the verification of the Knudsen's law of molecular streaming.

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Mercury vapour pressure at temperatures 7° to 25° C. The measuring appliance of the apparatus has been the phlegmatic liquid filled gauge of Bačkovský-Slavík.

The method and the procedure of measurement of mercury vapour pressure have been such that the results have been quite independent of the influence of certain inherent objectionable conditions, thereby rendering the measurement of mercury vapour pressure not only absolute but also precise. The attained precision, being high, enables one to test the validity of Knudsen's mercury vapour pressure measurements.

A comparison of the present results with those obtained by streaming method as well as with those obtained by directly measuring with the absolute gauge has shown that the results by streaming method are more precise than those obtained by measurement with the absolute gauge. By the confirmation of the present results with those obtained by streaming method, the Knudsen's law of molecular streaming has been verified.

Introduction. Measurement of the lowest attainable pressures of gases has certain obstacles which are not easy to overcome. In the measurement of these pressures, it is required to clear of any gas adhering to the walls of the enclosure and the gauge. This is usually done by thoroughly heating the enclosure as well as the gauge while speedily exhausting them by high vacuum pumps. It has been shown already by Shrader¹⁾ that such heat treatment, if sufficiently done, is capable of removing the gases as well as the vapours adhering to the surfaces of the instruments. But such heating and the subsequent cooling the gauge back to the normal temperature cause it to act as a „getter“ in as much as the walls reabsorb the gases in the enclosure. In the former case our pressure readings are higher and in the later case they are lower in value than that of the real pressure.

In the case of the measurement of the lowest attainable vapour pressures there are more obstacles and they are even

¹⁾ Shrader: Phys. Rev., 18 (1919), 434.

more difficult to overcome than in the case of the measurement of the highest attainable gaseous pressure. The only gauge which is claimed to be capable of measuring low vapour pressures absolutely is the original model of Knudsen,²⁾ whose function is based on the radiometric action. But it is by no means easy to construct a true absolute gauge as that of Knudsen, for it is very difficult to realise a very small distance between an oscillating system and a fixed plate. In almost all the later models, constructed for certain practical purposes, the mentioned distance is not small, unlike that in the original model of Knudsen, compared with the mean free path. Since Knudsen's equations apply only when the distance between the fixed and the oscillating systems is considerably small compared with the mean free path, these later models, though based on the radiometric action, cannot be used as absolute manometers. West³⁾ has shown that when the distance between the oscillating system and the fixed system is not small compared with the mean free path, the nature of the gas effects the functioning forces. As such the later models of radiometer gauges are lack of "absoluteness".

With the absolute gauge, it is required to measure quite precisely the temperature of not only the hot plate system but also that of both the sides of the cold plate system. Knudsen made provision for the temperature measurement of even both the sides of the cold plate system. It is however very impracticable to make such a provision for the temperature measurement of both the sides of the suspended system which at the same time can permit heat treatment to clear of any gas sticking to the surfaces. If the heat treatment is not properly done, the pressure measurement cannot be precise. If suitable provision is not made for the temperature measurement of both the sides of the suspended system, the temperature of the suspended system cannot be directly measured. In the absence of the direct measurement of the actual temperature of the cold plate system, as in the case of most of the radiometer gauges, there is always a certain amount of uncertainty in the values of the pressure measurements. Therefore they can be deemed to be neither absolute nor precise. In spite of all these objectionable and difficult features, Knudsen somehow constructed an absolute gauge and measured with it the saturation vapour pressures of mercury at temperatures ranging from -10° to 25° C.⁴⁾

Prior to the invention of the mentioned absolute gauge,

²⁾ Martin Knudsen: *Ann. der Phys.*, **32** (1910), 809—842.

³⁾ G. D. West: *Proc. Phys. Soc.*, **27** (1916), 259; **31** (1919), 278; **32** (1920), 166; **33**, (1920), 222.

⁴⁾ M. Knudsen: *Ann. der phys.*, **32** (1910), 838.

Knudsen also gave an ingenious method for the measurement of the saturation vapour pressure of mercury, based on the application of the Knudsen's law of pure and steady molecular streaming through a tube wherein a plate with a circular hole is fixed, which is given by⁵⁾

$$G = \sqrt{e} \cdot \frac{p' - p''}{W_1 + W_2} \cdot t \text{ or } p' - p'' = \frac{G(W' + W'')}{\sqrt{e_1} \cdot t}$$

where G is the mass of gas or vapour, e_1 the density at a pressure of 1 dyne per cm^2 , W_1 and W_2 the "resistance" of the tube and the opening respectively and t the time through which the gas or vapour streams down through the tube system. He arranged his apparatus in such a way that the mercury vapour streams down a tube through a small hole and becomes condensed in a cold graduated bulb. He determined the mass of vapour streamed for a time t by weighing the distilled mercury. From the dimensions of the tube and the hole he determined the "resistance" W_1 and W_2 . As the initial pressure was very low, its value could be taken as zero. Introducing the experimentally determined values of G at different temperatures in the equation 1, Knudsen determined the saturation vapour pressure of mercury from 0° upto $154,4^\circ \text{C}$. Having compared his results with the theoretically calculated values as well as with the results of the former authors, he estimated the precision of his measurements by his method. The estimated precision was found to be nearly 0,5% which may be considered the highest attainable precision by any method of measurement of low vapour pressures. Knudsen's results however have not been so very well verified so as to enable us to confirm to his verification of the law of steady molecular streaming by direct and absolute measurements. This method which would serve more to verify the law of steady pure molecular streaming rather than to directly measure vapour pressures, though very precise, is indirect, slow in operation and does not seem very practicable for the low vapour measurements.

Besides the said Knudsen's direct measurements of low vapour pressure of mercury with the absolute gauge, all investigations on low vapour pressures have been carried by indirect methods involving rate of diffusion, viscosity, ionic conductivity etc. which are in a way based upon assumptions concerning the structure and degree of association of the vapour. The only direct and the most suitable method with which saturation pressure of mercury could be measured is by means of an apparatus in conjunction with a McLeod gauge, known as tensimeter, elaborated

⁵⁾ Martin Knudsen: Ann. der Phyk., 29 (1909), 179—192.

and developed by Hickman.⁶⁾ It has been used for the measurement of vapour pressures ranging from atmospheric pressure to 0,05 mm Hg. He points out that his apparatus does not provide satisfactory means for determining vapour pressures lower than the mentioned limit. This method however extends the lower limit than ordinarily recorded and is quite practicable and more convenient than that of Knudsen's absolute manometric measurements of mercury vapour pressure. With this method, Hickman measured saturation vapour pressures of some high boiling organic liquids as well as that of mercury. As far as mercury is concerned, the lowest limit of his measurement of the saturation vapour pressure was 0,08 mm Hg which corresponds to the vapour pressure at a temperature of 80° C.

Now it may be mentioned that the required experimental equipment for the measurement of vapour pressure by the indirect method of molecular streaming as well as the Hickman's tensimeter permit a more suitable heat treatment for clearing of the surfaces from the occluded and the surface gases than the Knudsen's absolute gauge, because the surfaces of the later are more complicated than those of the former. The liquid filled gauges, in this respect, are very advantageous as the heat treatment for degassing need not be so high as in the case of the instruments with the metallic parts, where the heat treatment for degassing must be such that it would, in coming back to normal temperature, act as a "getter".

Having realized that the saturation vapour pressures of some of the high boiling organic liquids are much lower than that of mercury and that the coefficient of friction of these liquids is much lower than that of mercury with the walls of the glass tubes, Hickman and Sanford⁷⁾ conceived the use of some of these high boiling organic ones as gauge filled liquids. Consequently with one of these liquids whose vapour pressure is very low, they constructed a gauge⁷⁾ the precision of which was said to be 0,001 mm Hg. They did not however use their gauge for the measurement of vapour pressure.

Subsequently some authors made use of these phlegmatic liquids in their gauges. But none seemed to have attempted to measure vapour pressures with their gauges. Backovsky and Slavik⁸⁾ however have shown that certain kinds of the phlegmatic liquid filled gauges could be utilized for the measurement of

⁶⁾ K. C. D. Hickman: Jour. Phys. Chem., **34**, (1930), No. 3, 627—636.

⁷⁾ K. C. D. Hickman and C. R. Sanford: Jour. Phys. Chem., **34**, (1930), No. 3, 651.

⁸⁾ J. M. Backovsky and J. B. Slavik: Čas. pro přest. mat. fys., **66** (1936), 67—84.

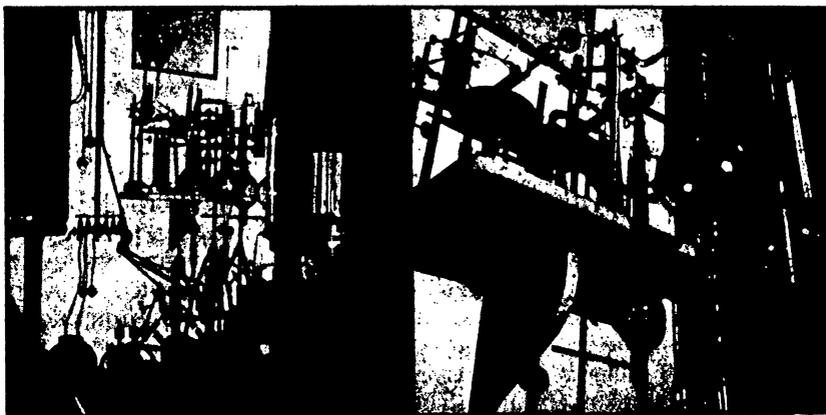
vapour pressures by actually measuring the saturation vapour pressure of mercury at 24° C. From the description of their form of the gauge, it seemed that it could be possible to absolutely measure with it the low vapour pressures of mercury very precisely, for the limit of observation depends upon certain factors which are technically possible to adjust. In using this gauge for the measurement of the saturation vapour pressure of mercury, certain practical difficulties however have been encountered and in trying to surmount them a certain procedure has been taken so as to utilize the gauge for the absolute and the precise measurement of the saturation vapour pressures of mercury from 25° C down to 7° C. To the requirements of the mentioned procedure, we have constructed our equipment, shown in the Fig. 1, so as to increase the sensitivity and thus raise the precision of the measuring appliances of our equipment.

The equipment and experimental procedure.

The equipment consists of a double chambered vacuum enclosure, exhausted by a high speed paraffin condensation pump, which is backed by a suitable auxiliary rotary pump, two phlegmatic liquid filled gauges, joined to either one of the chambers of the vacuum enclosure, which can be simultaneously used for pressure measurements to minimize the accidental errors, a McLeod gauge joined with one of the chambers by means of a side tube not only to measure the pressure of high vacuum before the commencement of the experiment but also to serve as a source of mercury vapour, a mercury bulb, as an auxiliary source of mercury vapour, connected to the vacuum chamber by means of a tube which can be either closed or opened according to the requirements and three thermometers to record the inner and the outer temperatures of the double chambered vacuum enclosure. When required, the vacuum enclosure can be easily converted into mercury vapour reservoir by opening it to the activated and functioning sources of mercury vapour. The two gauges, one filled with Triocresylphosphate, and the other with Butyl benzyl phthalate, form the principal part of the equipment for measuring low vapour pressures of mercury. (Fig. 1.)

The entire equipment together with the two mentioned phlegmatic liquid filled gauges has been exhausted by means of a paraffin condensation pump. The obtained vacuum when measured by a McLeod manometer and tested by a high tension electrical discharge, has been found to be of a pressure lower than 10^{-6} mm Hg. The pump speed has been such that the presence of mercury vapour in the vacuum enclosures could not be detected

even when the connection between vacuum enclosure and the McLeod gauge or the mercury reservoir has been opened. In this state the readings of the two phlegmatic liquid filled gauges have been simultaneously taken. Again after once more closing the connection between the vacuum enclosure and the McLeod gauge or the mentioned mercury reservoir, the readings of both the phlegmatic liquid filled gauges have been again taken simultaneously. In both the cases the manometric readings have been found to be remaining stationary so long as the temperature in both the cases remained constant, thereby indicating that in both cases there has been no detectible presence of mercury vapour.



a

Fig. 1.

b

When the temperature of the apparatus is changed, we have however found a change in the readings of the said gauges. In order to ascertain whether or not the changes in the manometric readings have been due to the variation of the angles of inclinations of the manometers which could be caused by the dilatation of the stand of these gauges through the temperature variation, we have observed the angular inclinations of these gauges by viewing reflections of fixed positions in mirrors attached to each one of the gauges with a separate telescope. It is important that there has been no observable change in the said angular inclinations of the manometers due to temperature variations. There has been, however, a considerable change in the position of the meniscus with the change of temperature. When the variations of the positions of the meniscus of the gauge filled liquid with the changes of temperature ranging from 7° to 25° C

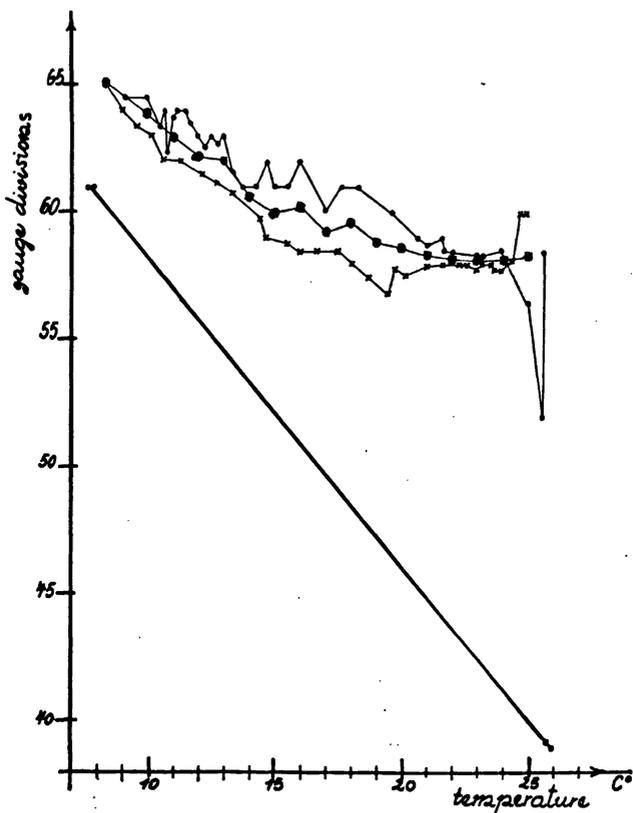
have been observed, they have been found to be of such magnitudes which would support a pressure of about 10^{-4} mm Hg in one manometer and 10^{-3} mm Hg in the case of the other manometer, filled with a different kind of phlegmatic liquid. Since these variations of the position of the meniscus of the gauge filled liquid are much greater than what could be expected from the considerations of the low saturation vapour pressure of each one of the gauge filled liquids at this temperature range, it can be stated that these changes which are unexpectedly great in value could be mainly due to the pressure of the products of cracking of these liquids during the heat treatment. We have found that even a careful heat treatment could introduce an error of the order 10^{-3} to 10^{-4} mm Hg and that the heat treatment would attack only the parts wetted by the liquids, especially the bulb part of the closed limb of the manometer.

We have found that even with this kind of heat treatment which would cause discrepancy in the pressure readings due to the pressure exerted by the products of cracking, it is possible to directly measure the true pressures by taking manometric zero positions for different temperatures. After thoroughly exhausting the whole vacuum enclosure together with the phlegmatic filled gauges, when we are sure that there has been no detectable presence of vapours and when the pressure of the attained vacuum is lower than 10^{-6} mm Hg, we have read at a certain temperature the position of the meniscus in the opened limb of each one of the manometers by means of a microscope. This reading of the position of the meniscus of each one of the manometers at the temperature is taken as the zero position of each one of the gauges for that particular temperature. We have changed the temperatures and for each temperature we have taken the zero positions. Thus we have actually determined the zero positions of each one of the phlegmatic filled gauges at temperatures between 7° C and 25° C.

In order to measure the inner and the outer temperatures of the apparatus, we have inserted one thermometer in the vacuum enclosure and a couple of thermometers outside quite close to the vacuum enclosure. It has been necessary to wait till the inner and the outer temperatures have come to equilibrium for fixing the zero positions of the manometers. Such waiting for temperature equilibrium causes considerable delay. We have waited for temperature equilibrium in the case of fixing the zero positions of the mentioned gauges at different temperatures. But we have not done so where it has not been quite so necessary.

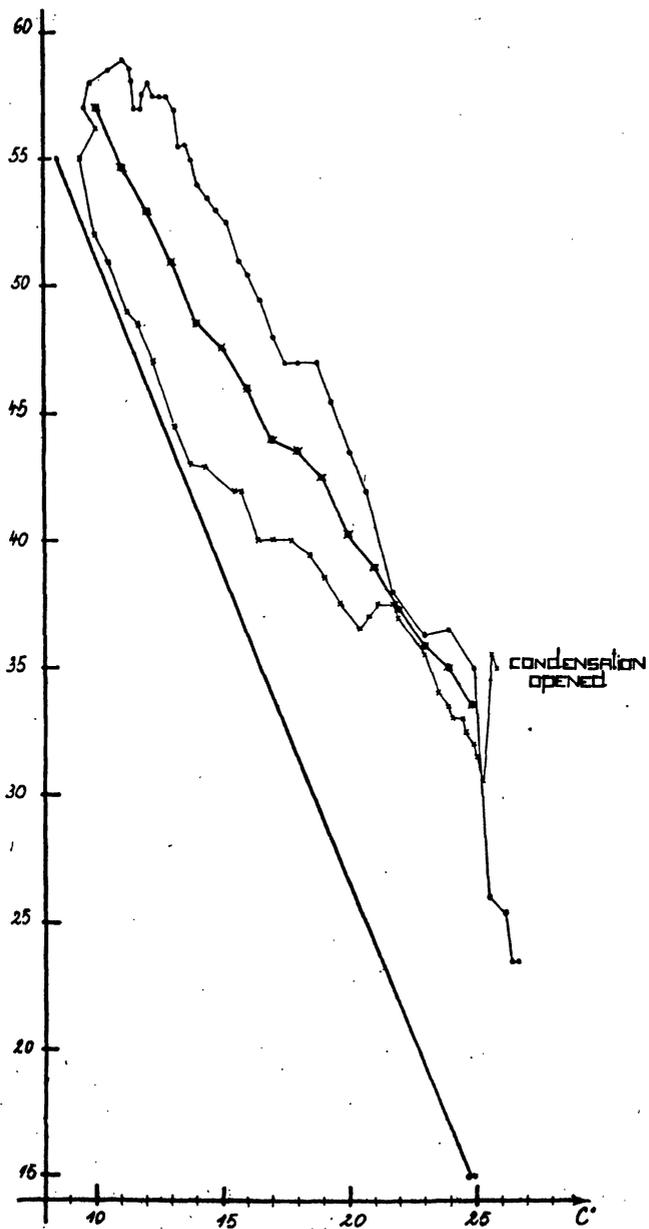
With this arrangement and after determining the zero positions of the said gauges as described above, we have measured the saturation vapour pressure of mercury at temperatures from 25° C

down to 7° C in the following manner. After introducing mercury vapour into the vacuum enclosure till complete saturation is attained, we have taken manometric readings from both gauges at different temperatures which can be seen from the graph I and the graph II. In the graph I, it can be noted that the zero



Graph I.

positions of one manometer at 25° C and 9° C are 42,5 and 61,0 divisions respectively and when the graphical positions of these two values are joined together we obtain the curve of the manometric zero positions for all temperatures between 9° C and 25° C. Also it can be seen that there are two series of manometric readings for saturation vapour pressure of mercury at the mentioned temperature range. The manometric readings of saturation mercury vapour pressure marked \cdot in the curves of the graphs Nos I and II, signify that these readings are those, taken



Graph II.

with the gradual lowering of temperature, while the rest that are marked in the curve are taken with the gradual rising of temperature. The rising and lowering of temperatures have been effected by fanning and regulated ventilation through windows in winter.

From the graphs I and II it can further be noticed that the curve of the readings with the lowering of temperature is slightly displaced from that of the readings with the rising of temperature through the same temperature-range in both the cases, so that we obtain two readings for each temperature through this range with a difference of 1, to 2 divisions for each given degree of temperature of the mentioned range. Such a difference can be explained by the fact that we have not waited until there is a temperature equilibrium in and out of our apparatus. We have however plotted a mean curve through the middle points of the mentioned curves at each position corresponding to every degree of temperature from 25° down to 10° C, and this gives the mean values of the manometric readings of the mercury vapour pressure at the mentioned temperature range. Similarly the graph II gives the mean values of the manometric readings at the same temperature range by the second phlegmatic liquid filled gauge.

The angle of inclination of the Triocreoylphosphate filled gauge is 1° 23' 27,5" and the specific gravity of this gauge filled liquid is 1.178 at 24° C. Each division of this gauge corresponds to 8.992×10^{-5} mm Hg. The angle of inclination of Butyl-benzyl phthalate filled gauge is 2° 43' 30". The specific gravity of this gauge filled liquid is 1.109 at a temperature of 20° C. Each division of this gauge corresponds to 8.661×10^{-5} mm Hg.

Now since each manometric division corresponds to 8.992×10^{-5} mm Hg in the case of Triocreoylphosphate filled gauge and 8.661×10^{-5} mm Hg in the case of Butyl-benzyl phthalate, the different divisions between the Zero-curve and the mentioned mean curve of each one of the manometers at any given temperature give the measured saturation vapour pressure of mercury by each one of the gauges. In this way we have obtained a separate series of measured values of the saturation vapour pressure of mercury at all degrees of temperature from 25° down to 10° C by each manometer and the two series of measurements by the gauge one and the gauge two are given separately in the third columns of the table 1 and table 2 respectively. Owing to differences of temperature in the different regions of the apparatus, there could be a slight influence of thermal efflux upon our readings. We have however corrected the readings for this influence and obtained the actual pressure values which are given in the final columns of the tables 1 and 2 and in the Ist and the IInd

columns of the table 6. We have further taken the mean of these two corrected values obtained separately by each of the two gauges for each degree of temperature and these mean values of corrected pressures are given in the last column of the table (6).

Table 1.

1. Tri-o-croeylphosphate filled gauge.

1 division = 8.992×10^{-5} mm mercury.

Saturation vapour pressure of mercury from 10° C to 25° C measured in the unit 10^{-3} mm Hg by the manometer 1.

Temperature	Divisions	Measured pressure	True pressure
10,0° C	4,8	0,432	0,440
11,0° C	5,9	0,531	0,543
12,0° C	6,4	0,575	0,589
13,0° C	7,5	0,674	0,690
14,0° C	7,2	0,634	0,648
15,0° C	7,9	0,712	0,731
16,0° C	9,2	0,827	0,852
17,0° C	9,6	0,863	0,890
18,0° C	11,0	0,989	1,021
19,0° C	11,5	1,034	1,070
20,0° C	12,5	1,124	1,166
21,0° C	13,5	1,214	1,262
22,0° C	14,5	1,304	1,358
23,0° C	15,6	1,403	1,463
24,0° C	17,0	1,529	1,598
25,0° C	18,3	1,646	1,723

It is very useful to record the vapour-pressure-temperature relation by plotting the logarithms of the pressures against the inverse of absolute temperature, for it enables us to easily judge the precision of the individual values. So we have plotted the individual values, given in the tables 1 to 4, obtained separately by the two gauges in the mentioned sort of graph III, so as to show the precision of our individual readings. For comparison the Knudsen's measurements of the saturation pressure of mercury at temperatures from 0° C to 25° C by the method of molecular streaming on the one hand and the measurements by the absolute gauge on the other have been plotted in the graph and they are marked with + and × respectively. For further comparison we have also plotted the mercury vapour saturation pressure values

Table 2.

2. Butyl-benzyl phthalate filled gauge.

1 division = 8.661×10^{-5} mm mercury.

Saturation vapour pressure of mercury from 10° C to 25° C, measured in the unit 10^{-3} mm Hg by the manometer 2.

Temperature	Divisions	Measured pressure	True pressure
10,0° C	5,8	0,502	0,511
11,0° C	5,9	0,511	0,521
12,0° C	6,5	0,563	0,575
13,0° C	7,0	0,606	0,620
14,0° C	7,5	0,650	0,667
15,0° C	8,7	0,754	0,774
16,0° C	9,5	0,823	0,847
17,0° C	10,0	0,866	0,893
18,0° C	11,9	1,031	1,064
19,0° C	13,3	1,152	1,191
20,0° C	13,5	1,169	1,211
21,0° C	14,8	1,282	1,330
22,0° C	15,5	1,342	1,395
23,0° C	16,5	1,429	1,488
24,0° C	17,5	1,506	1,571
25,0° C	19,0	1,646	1,720

Table 3.

1. Tri-o-creoylphosphate filled gauge.

1 division = 8.078×10^{-5} mm mercury.

Saturation vapour pressure of mercury from 7° to 8° C measured in the unit 10^{-3} mm Hg by the manometer 1.

Temperature	Divisions	Measured pressure	True pressure
7,1° C	4,1	0,336	0,345
8,0° C	5,05	0,409	0,420

for the temperatures from 0 to 25° C given in the international critical tables.*)

*) International Critical Tables of numerical data, Vol. 3, page 206, 1st Edition, (1928).

Table 4.

2. Butyl-benzyl phthalate filled gauge.
1 division = 7.856×10^{-5} mm mercury.

Saturation vapour pressure of mercury from 7° to 8° C, measured in the unit 10^{-3} mm Hg by the manometer 2.

Temperature	Divisions	Measured pressure	True Pressure
$7,1^{\circ}$ C	4,5	0,350	0,360
$8,0^{\circ}$ C	—	—	—

Table 5.

Mean values of the saturation vapour pressure of mercury from 7° to 8° C, given in the unit 10^{-3} mm mercury.

Temperature	By Gauge I.	By Gauge II.	Mean pressure
$7,1^{\circ}$ C	0,345	0,360	0,353
$8,0^{\circ}$ C	0,420	—	0,420

Table 6.

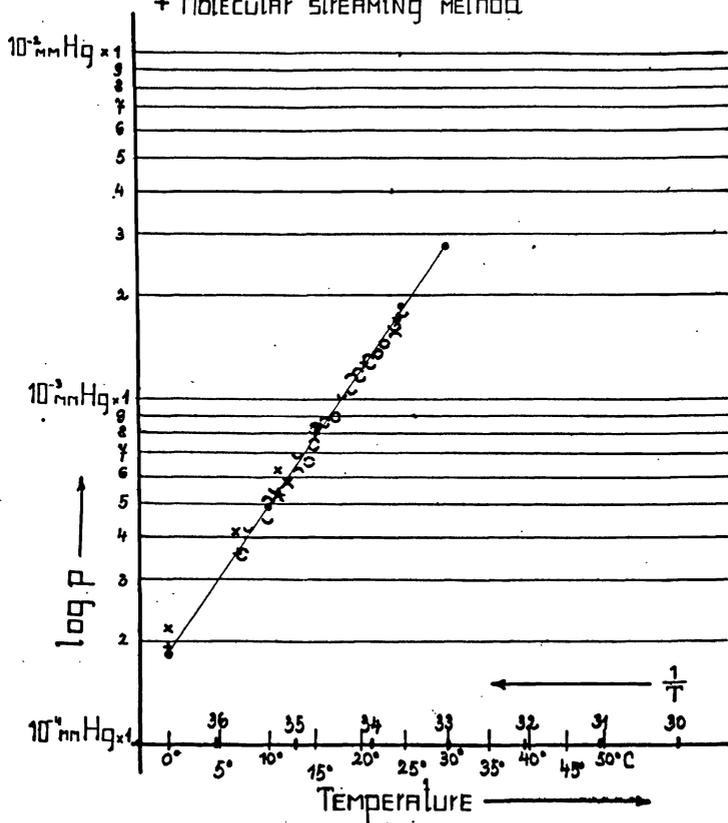
Mean values of the saturation vapour pressure of mercury from 10° C to 25° C, given in the unit 10^{-3} mm mercury.

Temperature	By Gauge I.	By Gauge II.	Mean pressure
$10,0^{\circ}$ C	0,440	0,511	0,476
$11,0^{\circ}$ C	0,543	0,521	0,537
$12,0^{\circ}$ C	0,589	0,575	0,582
$13,0^{\circ}$ C	0,690	0,620	0,655
$14,0^{\circ}$ C	0,648	0,667	0,658
$15,0^{\circ}$ C	0,731	0,774	0,753
$16,0^{\circ}$ C	0,852	0,847	0,850
$17,0^{\circ}$ C	0,890	0,893	0,892
$18,0^{\circ}$ C	1,021	1,064	1,042
$19,0^{\circ}$ C	1,070	1,191	1,130
$20,0^{\circ}$ C	1,166	1,211	1,188
$21,0^{\circ}$ C	1,262	1,330	1,296
$22,0^{\circ}$ C	1,358	1,395	1,376
$23,0^{\circ}$ C	1,463	1,488	1,475
$24,0^{\circ}$ C	1,598	1,571	1,584
$25,0^{\circ}$ C	1,723	1,720	1,722

Critical observations.

It can be seen in our graph III that our individual measured values do not show any systematic variation from the calculated values given in the International Critical Tables for the range of

- Data from International critical tables
- ∨ Tri-o-cresylphosphate filled gauge
- ~ Butyl-benzyl phthalate filled gauge
- × Knudsen's Absolute gauge
- + Molecular streaming method



Graph III.

temperature from 0° C to 25° C in the limits of the obtained precision. The cause of the small differences between the readings of the two gauges is to be attributed to the differences in temperature equilibrium. The individual differences, so caused, are

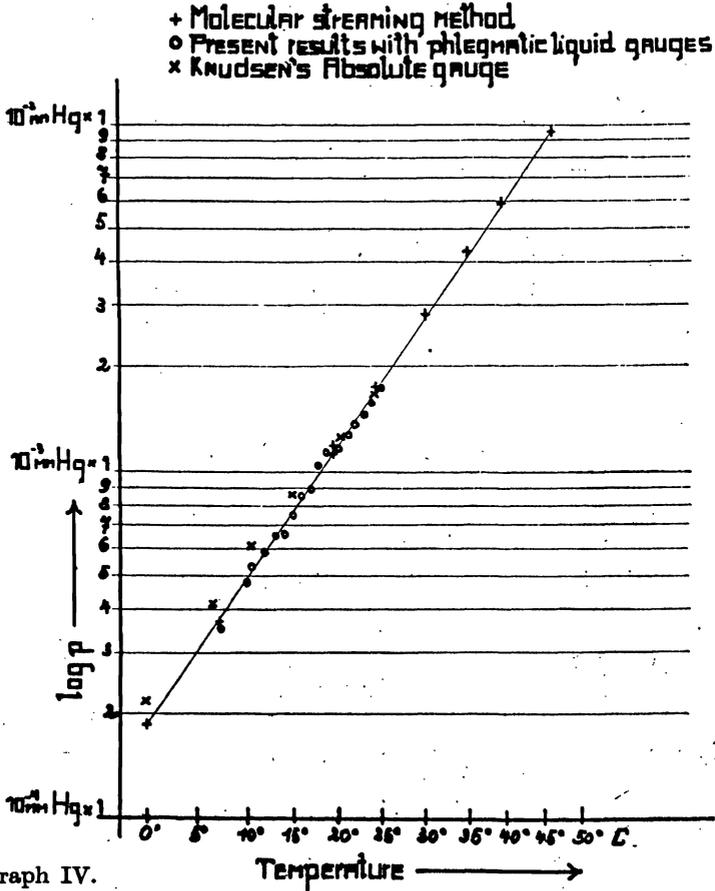
irregularly higher in some cases and in some lower than those of the International Critical Tables and the measurements of one gauge are not systematically higher or lower than those of the other, so that the mentioned differences must be considered to be accidental. From these accidental minor deviations, the limit of precision of our absolutely measured values of the vapour pressure of mercury with the mentioned phlegmatic liquid filled gauges, can be easily ascertained.

We have taken the manometric readings at every two minutes at a constant temperature between 7° and 8° C for about half an hour while keeping the reservoir fully opened to both the functioning sources of mercury vapour. During the period the gauge readings have been constant thereby indicating that the reservoir has been full to saturation with mercury vapour. These saturation vapour pressure readings at temperatures 7° to 8° C given in the tables 3, 4, and 5 fall on the pressure-temperature-relation straight line of our values of vapour pressures of mercury at all other degrees of temperature till 25° C. Therefore it can be considered that at each one of the rest of our pressure measurements, the reservoir has been full to saturation with mercury vapour.

The two mercury vapour pressure values at $7,1^{\circ}$ C, obtained by the two mentioned phlegmatic liquid filled gauges do not differ more than by nearly 5%. These pressure values as well as those of ours at temperatures $11,1^{\circ}$, $15,7^{\circ}$, $20,6^{\circ}$, and $24,4^{\circ}$ C agree fairly well with the values for the same range of temperature obtained by the method of molecular streaming. Similarly the vapour pressure value for 0° C, extrapolated from our measurements at other temperatures agrees with the value for the same temperature obtained by the said molecular streaming method. But the pressure value for 0° C obtained by measuring with the Knudsen's absolute gauge is higher by 18% than that by the molecular streaming method as well as our mentioned extrapolated value. This difference can be said to be much higher than the limit of our attained precision. The other values of the vapour pressure measurements by the absolute gauge are in fact systematically higher than our values as well as those by the method of molecular streaming method and are per centually increasing with the increasing temperature.

Since the measurement of the saturation vapour pressure with the absolute gauge is direct, the above mentioned difference of about 18% between the pressure values obtained by the direct measurement with the absolute gauge and those obtained indirectly by the method of molecular streaming might lead one to the conclusion that the streaming method and the law of pure

and steady molecular flow, given in the expression 1 (page 3a), on which the method is based, are not quite rigorous. To show that this sort of conclusion is not valid, we plot our mean pressure values given in the last columns of the tables (5 and 6), those obtained by the method of molecular streaming and finally also the



Graph IV.

pressure values obtained by the direct measurement with the absolute gauge in the graph No. IV, recording the pressure-temperature-relation for general comparison and further judgment. In the graph IV, it can be seen that the curve of our directly measured absolute mercury-vapour-pressure values, in the limit of our attained precision, coincide on the one hand precisely with the pressure values obtained by the indirect method of molecular

streaming and on the other considerably differ from the values obtained by the direct measurement with the Knudsen's absolute gauge.

In this connection we may point out that the values of the constants A and B , occurring in the equation¹⁰⁾

$$\log_{10} p = - 52,23 \frac{A}{T} + B, \quad (2)$$

calculated from our directly measured absolute pressure values of mercury vapour are $A = 61,943$, and $B = 8,1166$. Now on introducing these values and the absolute temperature value for 0°C in the above mentioned equation (2), we obtain $0,18433 \times 10^{-3} \text{ mm Hg}$ as the saturation vapour pressure of mercury at a temperature of 0°C , calculated from our directly measured values for other temperatures. This value $0,18433 \times 10^{-3} \text{ mm Hg}$, calculated from our values of the constants A and B , for the temperature of 0°C indeed agrees quite well with the value $0,1846 \times 10^{-3} \text{ mm Hg}$ for the same temperature, obtained by the streaming method and differs actually by nearly 18% from the pressure value for 0°C obtained by the direct measurement with the absolute gauge.

Thus our directly and absolutely measured, calculated, as well as our extrapolated values, in agreeing well with the results obtained by the method of molecular streaming and in widely differing from the values by the absolute gauge, show that the former are more precise than the later mentioned values by the absolute gauge. We may go even a step further and say that the pressure-values obtained by direct measurement with the absolute gauge are in fact not so precise as those of ours as well as those obtained by molecular streaming, because the pressure-values with the Knudsen's absolute gauge, being corrected empirically, have such corrections which, as Knudsen pointed out on the page 838, *Ann. der phys.*, volume 32 (1910), would introduce an uncertainty in the pressure values. So our direct and absolute measurements, in disagreeing with the results by the absolute gauge and in thoroughly confirming with the results obtained by the method of molecular streaming in a way verify the method and the law of molecular streaming on which the method is based. In this connection it may be pointed out that the mercury vapour saturation pressure value for 0°C , $0,1846 \times 10^{-3} \text{ mm Hg}$, obtained by the streaming method or our value $0,18433 \times 10^{-3} \text{ mm Hg}$, obtained from the mentioned constants A and B derived from our actually measured values, must be rightly taken as the standard value to be used as the constant to calculate the values for the

¹⁰⁾ International Critical Tables of Numerical Data, Volume III, 204.

mercury vapour pressure-temperature-relation curve, and also to calibrate the ionization gauge for the relative measurements of vapour pressure of mercury at low temperatures as was done in the case of the modified ionization gauge with which Poindexter¹¹⁾ measured mercury vapour pressure at low temperatures.

In concluding this work, I beg to offer my heartiest thanks to Prof. Dr. Václav Dolejšek Esq. not only for the arrangements which he has made for my Research in the Spectroscopical Institute Laboratory of the Charles University but also for his unbounded kindness which he has been pleased to so lavishly bestow upon me during my stay in this kind and hospitable land of the Czechs. My thanks are due to my Czech friends and fellow research scholars for their kind help during the research. Finally it is my great privilege to tender my deepest gratitude and gratefulness to His Highness Sri Maharaja Sir Narendra Shah, the ruling chief of Tehri-Garhwal State (India) for His Highness's interest in my philosophic and scientific pursuits.

Absolutní měření napětí rtuťových par za teploty 7° až 25° C a ověření Knudsenova zákona o molekulárním proudění.

Obsah předešlého článku.

Autor podává přímé absolutní měření tlaku par rtuti v rozmezí teplot 7° až 25° C, které v laboratoři lze získati bez zvláštních opatření (na př. v zimě při normálním topení a při otevření oken). Absolutní měření tlaku par Hg v tomto oboru bylo dosud docíleno přímo Knudsenem, jeho absolutním manometrem, a nepřímě (rovněž absolutně) rovněž Knudsenem, za užití jeho vzorců pro molekulární proudění.

Autor používá absolutního manometru s flegmatickou kapalinou, který udali Bačkovský-Slavík. Propracováním postupu pracovního, na př. vyloučením možného vlivu krakování kapaliny manometru, zavedením kontroly manometru a vyloučením vlivu činitelů, které vždycky s tímto manometrem jsou spjaty a omezují přesnost a absolutnost výsledků, docíljuje autor takové přesnosti, že může porovnáním obdržených výsledků ukázati, zda z Knudsenových měření jsou správné jeho výsledky pomocí nepřímé metody za užití zákonů molekulárního proudění, či výsledky pomocí absolutního manometru. Výsledky obdržené pomocí těchto Knudsenových metod liší se asi o 20%.

Výsledky autora, udané v této práci, souhlasí v rozmezí 2 až 4% s Knudsenovými hodnotami obdrženými pomocí metody molekulárního proudění.

¹¹⁾ F. E. Poindexter: Phys. Rev., 26, (1925), 859—868.

Tim jsou verifikovány Knudsenovy vzorce pro molekulární proudění přímým absolutním měřením. Pokud se týče výhodnosti v této práci použitého manometru typu Bačkovský-Slavík k měření tense par, je nesporné, že při stejné preciznosti absolutního měření je týž značně výhodnější, než aplikace nepřímé absolutní metody Knudsenovy, jejíž jednotlivé měření trvá na př. 13 dnů.

Praha, Spektroskopický ústav Karlovy university.

Foto a kresby S. Jnanananda. - Archiv JČMF.

Absolute Messung der Quecksilberdampfspannung für Temperaturen 7°—25° C und Bestätigung des Knudsen'schen Gesetzes der Molekularströmung.

(Inhalt des vorstehenden Artikels.)

Der Autor gibt direkte absolute Messungen der Quecksilberdampfspannung im Temperaturbereich von 7°—25° C, welche im Laboratorium ohne besondere Vorkehrungen zu erreichen sind (z. B. im Winter bei normaler Heizung und bei geöffneten Fenstern). Die absolute Messung der Hg-Dampfspannung in diesem Gebiet wurde bisher von Knudsen direkt mit seinem absoluten Manometer und indirekt (ebenfalls absolut) unter Benutzung seiner Formeln für die Molekularströmung vorgenommen.

Der Autor benutzt das absolute, mit phlegmatischen Flüssigkeiten gefüllte Manometer nach Bačkovský-Slavík. Durch Ausarbeitung des Arbeitsgangs, z. B. Eliminierung des möglichen Einflusses des Crackens der Manometerflüssigkeit, und Ausschluß des störenden Einflusses der immer mit diesem Manometer verbundenen Faktoren, welche die Genauigkeit und den absoluten Charakter der Resultate einschränkten, erzielt der Autor eine solche Genauigkeit, daß er durch Vergleich der erzielten Resultate zeigen kann, ob Knudsen's Resultate nach der indirekten Methode unter Benutzung der Molekularströmung, oder die mittels des absoluten Manometers erzielten richtig sind. Die mittels dieser beiden Methoden von Knudsen erzielten Resultate unterscheiden sich ungefähr um 20%.

Die in dieser Arbeit angeführten Resultate des Autors stimmen innerhalb eines Spielraums von 2—4% mit Knudsen's Resultaten nach der Methode der Molekularströmung überein.

Dadurch wurden Knudsen's Formeln für die Molekularströmung nach einer direkten absoluten Methode verifiziert. Was die Vorteile des bei dieser Arbeit benutzten Manometertyps Bačkovský-Slavík betrifft, ist dieser zweifellos bei gleicher Genauigkeit vorteilhafter als die Anwendung der indirekten absoluten Methode Knudsen's, deren einzelne Messungen z. B. 13 Tage dauern.