A SIMPLE MANOMETER FOR MEASURING LOW PRESSURES[1]

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According to the kinetic theory of gas, the heat conductivity of a gas is independent of its pressure. This fact was verified experimentally by observing the cooling velocity of a body which is kept in the gas. Thus the time which is required to cool from a given temperature to another under a constant condition, is independent of the pressure of the surrounding gas. But this rule holds only within a limited range of pressures. Under high pressures it is disturbed by the convection of gas and by other phenomena. And at the pressures lower than few millimetres of mercury, longer time is required for the cooling of the same temperature range under the same condition. This fact was first observed by Kundt and Warburg,[2], and was attributed to the discontinuity of the temperature gradient, which grows prominent at the boundary of the solid and gas, as the pressure diminishes.

Such a behavior of rarefied gas is sometimes utilised as the measure of its pressure. Pirani's manometer[3] and Rohn's manometer[4] belong to this type. Since then many improvements were reported[5]. The manometers of this type do not directry show the pressure, as Mc Leod manometer does, so we must calibrate them with known pressures. They are, however, free from mercury vapour, the existence of which will prevent the correct reading of the pressure, and moreover proves to be a hindrance to the perfect evacuation. Another great defect of Mc Leod manometer is that it cannot be used to measure the pressures of easily condensible vapours. For these reasons, in many cases, more complicated manometers such as those described above are used in place of the Mc Leod manometer.

Experimental. Here we describe another substitute for Mc Leod manometer, which is more simple and far less expensive than all other manometers. The construction of it is shown by *M* in Fig. 1. A thermometer

(1) Read before the Chemical Society of Japan, April, 1924.
(2) Kundt and Warburg, *Pogg. Ann.*, **156** (1875), 177.
(3) Pirani, *Verh, d. D. Phys. Ges.*, **8** (1906), 686.
(4) Rohn, *Z. Electrochem., Sec.*, **20** (1914), 534.
(5) Hale, *Trans. Amer. Electrochem., Soc.*, **20** (1911), 234.
Sô, *Proc. Tokyo Math. Phys. Soc., 3rd. Series*, **1** (1919), 152.
Campbell, *Proc. Phys. Soc. Landon*, **33** (1921), 287.

is fixed in a tube, which is specially so constructed that it has long cylindrical mercury bulb, and graduated to indicate one tenth of a degree. The thermometer should not be deformed by pressure change, and it is more prefarable that it is as sensitive as possible. These two contradictory requirements considerably restrict the sensitiveness of this manometer.

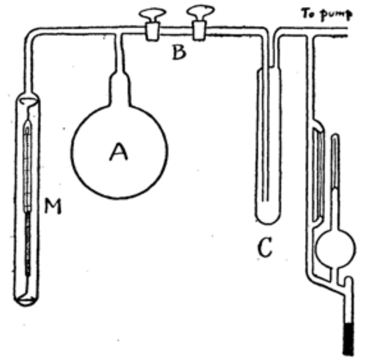

Fig. 1.

Now this apparatus, as already described, must be calibrated with known pressures. The pressures below to few tenth of a millimetre were compared with a Mc Leod manometer. For the pressures lower than these, a pipette system has been used which is shown in Fig. 1. The volumes of the spaces $M+A$ and B are known. At first the spaces A, B and M were thoroughly evacuated and then charge B with a gas of known pressure, and let it expand into A, M and B. As these volumes are known we can easily calculate the pressure after expansion of the gas. During evacuation the mercury trap C is cooled by liquid air to prevent the invasion of mercury vapour into the system. At a known pressure, the cooling velocity of the thermometer is measured by the following manner.

At first, M is warmed, and then suddenly envelop it with a bath of lower constant temperature. Now the thermometer begins to cool, and the time required to cool from a given temperature to the other is measured. It may be convenient to choose 0°, of melting ice, for the temperature of the bath. But in the present experiment, as the graduation of thermometer was from 30° to 42°, the cooling bath of 25° was used, and measured the time required to cool the thermometer from 39° to 32°. Limiting the range of the operating temperature narrower, we can well express the cooling velocity with the Newton's law of cooling, consequently we can easily calculate the requiring time even when we failed to measure the time of cooling for the given temperature range or when the thermostat was not exactly fixed at 25°. The Newton's law is

$$-\frac{dT}{dt} = k'(T-T_0), \quad \cdots\cdots(1)$$

or

$$t = k' \log \frac{T_1-T_0}{T_2-T_0}, \quad \cdots\cdots(2)$$

where t is the time required to cool from a temperature T_1 to another temperature T_2, T_0 is the temperature of the bath and k' is a constant depending on the pressure.

The cooling times obtained under various pressures are plotted against pressure in Fig. 2. As each gas has its own heat conductivity, different curves are obtained for different gases. The curves given are those for air and hydrogen.

If such curves were drawn for an apparatus, we can use it as a manometer. Now to construct these curves we must make troublesome measurements. But as is shown in the following pages, if we use a thermometer of long cylindrical mercury bulb, and limit the operating temperature range narrow enough, this pressure-time relation can be expressed in the following form:

$$p = k\ \frac{t_0 - t}{t - t_{760}} \qquad \cdots\cdots\cdots\cdots(3)$$

where t is the cooling time when the pressure is p, t_0 and t_{760} are the cooling times for the highest vacuum

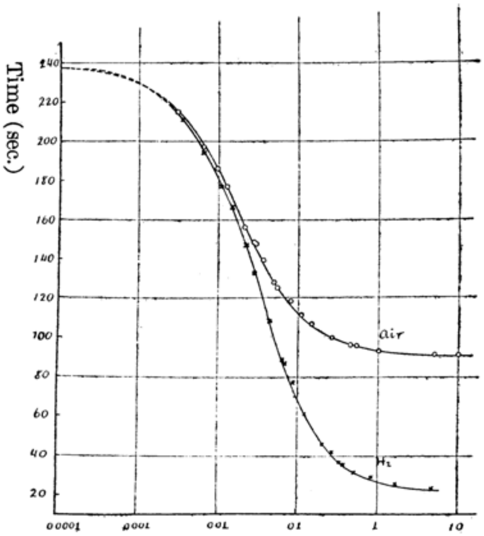

Fig. 2. Pressure (mm. in log. scale)

Air			Hydrogen		
p mm.	t sec.	$k = p\frac{t - t_{760}}{t_0 - t}$	p mm.	t sec.	$k = p\frac{t - t_{760}}{t_0 - t}$
760.	90.5 ($=t_{760}$)		770.	20.9 ($=t_{760}$)	
250.	90.5		223.	20.9	
26.	90.5		50.	21.0	
15.5	90.6		18.	21.3	
5.0	90.9		5.0	22.6	
1.8	91.0		1.62	25.1	
1.01	92.8		0.78	29.0	0.0295
0.52	95.5	0.0183	0.55	31.8	0.0291
0.43	95.9	0.0172	0.382	36.3	0.0292
0.262	100.0	0.0181	0.380	36.7	0.0299
0.145	107.2	0.0169	0.265	42.6	0.0296
0.108	110.7	0.0171	0.222	41.5	0.0285
0.0809	118.0	0.0188	0.124	61.0	0.0282
0.0540	124.2	0.0160	0.0860	76.5	0.0296
0.050	127.7	0.0186	0.0660	83.8	0.0285
0.0375	139.0	0.0185	0.0645	87.3	0.0286
0.0280	147.5	0.0177	0.0430	108.2	0.0290
0.0270	148.0	0.0173	0.0271	132.9	0.0290
0.0212	156.0	0.0171	0.0215	140.9	0.0267
0.0124	177.0	0.0177	0.0143	165.3	0.0285
0.00934	185.7	0.0172	0.0106	177.0	0.0274
0.00623	197.4	0.0168	0.00714	194.1	0.0285
0.00312	210.0	0.0133	0.00357	210.9	0.0255
0.0000	237.5 ($=t_0$)	—	0.0000	237.5 ($=t_0$)	—
		mean 0.01759			mean 0.02874

and 760 mm. respectively and k is a constant depending upon the nature of the gas and the dimentions of the apparatus. The experimental results are shown in the above table, together the values of k calculated therefrom. The curves in Fig. 2 represent these results.

Theoretical. Smoluchowski[1] introduced a quantity γ under the name of "Temperatursprungskoeffizient", having the following relation,

$$T' - T = \gamma \frac{\partial T'}{\partial n} \cdots\cdots\cdots(4)$$

where T is the temperature of the solid at the boundary, T' is that of the gas contacting to it, n is a normal drawn at the boundary surface inwards to the gaseous space, and γ is a proportionality constant. He has known experimentally that the quantity γ is proportional to the mean free path of the gas. Now, as the mean free path is inversely proportional to the pressure p, we can express this relation as follows,

$$\gamma p = \text{constant} \cdots\cdots\cdots(5)$$

This shows that if p decreases γ becomes larger, consequently $T' - T$ becomes larger and $\frac{\partial T}{\partial n}$ smaller. Under the pressures higher than few millimetres γ is negligibly small, so we cannot find any difference botween T and T', and there exists no cause that prevents the heat transmission through the boundary.

Assuming that the cylindrical mercury bulb of radius r_1, and the outer tube of radius r_2 are coaxial, and moreover we consider another coaxial cylinder between them, whose radius is r. Then, as the bulb is long, we may assume that there is no heat loss from the ends of the bulb. The heat transmission at the side of cylinder takes place in two ways, a part by conduction, which depends upon the conductivity of the gas $\varkappa$. temperature gradient $(\partial T'/\partial r)$ at this point, and the surface area of this cylinder $2\pi rl$, the other part by radiation, which can be regarded to be propartional to the difference of the temperature of the thermometer and that to the bath $(T - T_0)$, when the range of the operating temperature is narrow, otherwiese it obeys Stefan-Boltzmann's law.

Now in a unit time the thermometer bulb will lose the heat quantity $-C\frac{dT}{dt}$, so the following relation will be obtained;

$$-C\frac{dT}{dt} = -\varkappa\frac{\partial T'}{\partial r} 2\pi rl + A'(T - T_0) \cdots\cdots\cdots(6)$$

(1) Smoluchowski, *Ann. d. Phys. u. Chem.*, **64** (1898), 101.

Comparing (6) with (1), we obtain,

$$-\frac{dT}{dt} = (B+A')(T-T_0) \quad \cdots\cdots(7)$$

where $A' = -\frac{A}{C}$, $B = -\varkappa 2\pi r l \frac{\partial T'}{\partial r}\frac{1}{C}\frac{1}{T-T_0}$, and $k' = B+A'$.

As $\varkappa$, π, l, T_0 and C are constants, moreover T is constant at a moment, $\frac{\partial T'}{\partial r} r$ must also be constant at the moment, or

$$r\frac{\partial T'}{\partial r} = a \quad \cdots\cdots(8)$$

This expression shows the distribution of temperatures of the gas from r_1 to r_2 at that moment; and the difference of the temperatures at r_1 and r_2 is given by

$$T'_{r_1} - T_{r_2} = a \log \frac{r_1}{r_2} \quad \cdots\cdots(9)$$

From the relation (4)

$$\left.\begin{aligned} T'_{r_1} - T &= \gamma\left(\frac{\partial T'}{\partial r}\right)_{r_1} \\ T'_{r_2} - T_0 &= -\gamma\left(\frac{\partial T'}{\partial r}\right)_{r_2} \end{aligned}\right\} \quad \cdots\cdots(10)$$

Comparing these with (8), we get

$$\frac{T'_{r_1} - T}{\gamma} r_1 = \frac{T_0 - T'_{r_2}}{\gamma} r_2 = a$$

or

$$\left.\begin{aligned} T'_{r_1} - T \quad &= a\gamma\frac{1}{r_1} \\ T_0 \quad - T'_{r_2} &= a\gamma\frac{1}{r_2} \end{aligned}\right\} \quad \cdots\cdots(11)$$

From (9) and (11) we obtain,

$$T_0 - T - a\log\frac{r_1}{r_2} = a\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

or

$$a = \frac{T_0 - T}{\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \log\frac{r_1}{r_2}} \quad \cdots\cdots(12)$$

Then

$$B = -\frac{\varkappa 2\pi l}{C}\frac{1}{\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \log\frac{r_1}{r_2}} \quad \cdots\cdots(13)$$

By equation (5), this can be written in the form :

$$B = \frac{1}{\frac{a}{p}+b} \quad \cdots\cdots(14)$$

where $a = \left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{C}{2\pi l}\times$constant, and $b = \log\frac{r_1}{r_2}\frac{C}{\varkappa 2\pi l}$.

Now the integral form of (7) is

$$\log\frac{T_1'-T_0}{T_2'-T_0} = (B+A')\,t \quad \cdots\cdots(15)$$

In the perfect vacuum no conduction takes place, so $B = 0$, therefore

$$\log\frac{T_1'-T_0}{T_2'-T_0} = A'\,t_0 \quad \cdots\cdots(16)$$

From (14), (15) and (16) we obtain,

$$\left(\frac{1}{t}-\frac{1}{t_0}\right)A'\,t = \frac{1}{\frac{a}{p}+b} \quad \cdots\cdots(17)$$

If p is larger than few millimetres of mercury, then the value of a/p may be neglected to b, and the following relation will be obtained,

$$\left(\frac{1}{t_{760}}-\frac{1}{t_0}\right)A'\,t = \frac{1}{b} \quad \cdots\cdots(18)$$

Substituting the value of b from (18) to (17),

$$\frac{1}{\left(\frac{1}{t}-\frac{1}{t_0}\right)A'\,t_0} = \frac{a}{p}\cdot\frac{1}{\left(\frac{1}{t_{760}}-\frac{1}{t_0}\right)A'\,t_0}$$

or

$$\frac{a}{p}A' = \frac{t_0}{t_0-t_{760}}\,\frac{t-t_{760}}{t_0-t}$$

Putting

$$k = \frac{t_0-t_{760}}{t_0}\,a.\,A'$$

in the above equation, we obtain the relation (3),

$$p = k\,\frac{t_0-t}{t-t_{760}}.$$

Summary.

A simple all glass manometer, which can be used for measuring the pressures from 0.1 mm. to 0.001 mm. has been described. The manometer

consists of a thermometer enclosed in a tube. The pressure measurement is done by measuring the time required to cool the thermometer from a given temperature to the other under a given condition. Using a thermometer of long mercury bulb and limiting the operating temperature range so narrow that the Newton's law of cooling holds, we get the following relation :

$$p = k\,\frac{t_0 - t}{t - t_{760}}.$$

This relation was well confirmed by experiments using the air and the hydrogen.

In conclusion I wish to express my hearty thanks to Prof. J. Sameshima, under whose guidance the present investigation was carried out.

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