DETERMINATION OF HIGH TEMPERATURE BY THE EFFUSION AND THE TRANSPIRATION OF GAS.

By Yohei YAMAGUCHI.

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The rates of flow of gases at high temperatures were studied by Emich(1) for the determination of gas densities. I have undertaken some experiments to test whether such a phenomenon can be utilized for the determination of high temperature or not.

1. The Relation between the Temperature and the Rate of Effusion. The apparatus used for the measurement of the rate of effusion is shown in Fig. 1. On the stem of a glass vessel resembling Ostwald's viscosimeter, two marks A and B were etched, the volume between them being about 100 c.c. After the bulb was filled with a certain quantity of petroleum of high boiling point (215–225°), the lower part of the vessel is immersed in a thermostat at 25°. T is a quartz tube having a small opening at its end through which the gas effuses and is placed in an electric furnace. When the temperature of the tube became constant, the stop-cock C is opened and a certain quantity of dry air is blown into the system by means of D in order to push

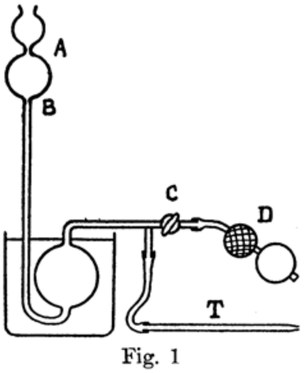

Fig. 1

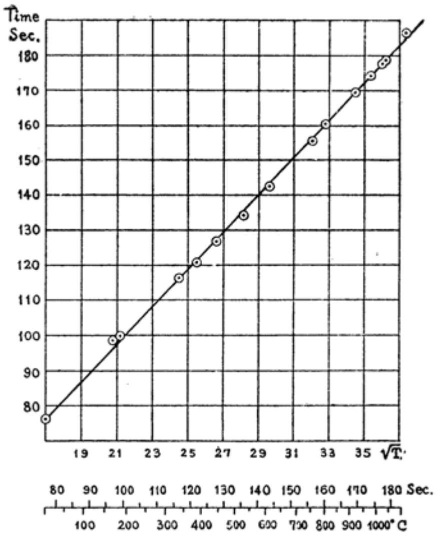

Fig. 2

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(1) Emich, *Monatsh.*, 24 (1903), 747; 26 (1905), 505.

up the petroleum above the mark A. Hereupon the stop-cock is closed and the time in which the petroleum falls down from A to B is measured. The relation between the measured time and the temperature is shown in Table 1⁽¹⁾.

TABLE 1.

Time in sec. (t)	Temp. C°.	Abs. temp. (T)	$\log T$	$\sqrt{T}$	$t_{calc.}$
76.4	17	290	2.4624	17.03	75.4
*115.8	328	601	2.7789	24.52	(115.8)
126.6	434	707	2.8494	26.59	127.0
142.9	605	878	2.9435	29.63	143.4
*170.0	922	1195	3.0774	34.57	(170.0)
177.9	1033	1306	3.1158	36.13	178.4
185.5	1125	1398	3.1456	37.40	185.3

Fig. 2 shows that there is a linear relation between the time (t) and the square root of the absolute temperature (T). Thus we can put,

$$t=a+b\sqrt{T} \quad \cdots\cdots\cdots\cdots (1)$$

Taking out two pairs of observed values and calculating the constants a and b, we obtain, $t=5.393\sqrt{T}-16.44$. The times of effusion are calculated by this equation from the observed temperatures and are shown in the last column of Table 1. The calculated times are in good agreement with the observed ones.

Theoretical. The definite quantity of gas corresponding to the volume between the marks A and B, will expand to a larger volume at the opening of the quartz tube where the temperature is high. Hence if the velocity of effusion be independent of temperature, the time of effusion (t) is proportional to the absolute temperature (T),

$$t \propto \text{volume} \propto T \quad \cdots\cdots\cdots\cdots (2)$$

Now the time of flow of gases by effusion under a given pressure difference is also inversely proportional to the mean velocity (v) of the gas molecules, and the mean velocity is, as is well known, proportional to the square root of the absolute temperature,

$$t \propto \frac{1}{v} \propto \frac{1}{\sqrt{T}} \quad \cdots\cdots\cdots\cdots (3)$$

Combining (2) and (3), we have,

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(1) More detailed data were published in the *Journal of the Chemical Society of Japan*, **43** (1922), 1.

$$t \propto \sqrt{T}\,, \qquad \text{or} \qquad t = b\sqrt{T} \cdots\cdots\cdots\cdots\cdots (4)$$

where b is a constant. The constant a in the empirical equation (1) may be considered to be a correction term to the equation (4) obtained by such a simple deduction.

2. The Relation between the Temperature and the Rate of Transpiration. High temperatures can also be determined by measuring the rate of transpiration of gases through a capillary tube of quartz. The apparatus employed for the purpose is similar to that used above, excepting that the quartz tube for effusion is now replaced by another quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. Some of the data obtained from the experiments are shown in Table 2.

TABLE 2.

Time in sec. (t)	log t	Temp. C°.	Abs. temp. (T)	log T	$T_{\text{calc.}}$
61.0	1.7853	20.5	293.5	2.4676	283
79.4	1.8998	125.5	398.5	2.6004	395
* 94.2	1.9741	200.2	473.2	2.6751	478
116.7	2.0671	333	606	2.7822	599
*151	2.1790	487	760	2.8808	767
212	2.3263	739	1012	3.0051	1025
*241	2.3820	848	1121	3.0496	1132
264.2	2.4219	929	1202	3.0799	1211
300	2.4771	1046	1319	3.1202	1321

The value of log T can well be represented by an equation of the second order of log t, thus

$$\log T = a + b \log t + c (\log t)^2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

Evaluating the constants a, b and c from three data marked with asteriscs in Table 2, we get the following empirical equation,

$$\log T = -1.0967 + 2.7376 \log t - 0.4178 (\log t)^2 \cdots\cdots (6)$$

The values of $T_{\text{calc.}}$ in Table 2, which were obtained from this equation, are in good agreement with the observed values.

3. The Relation between the Temperature and the Pressure of Gas Transpirating at a Definite Rate. The temperature of transpirating gas can also be determined by measuring the pressure necessary to keep a constant rate of flow of the gas. The apparatus shown in Fig. 3 was used for the purpose. If water is allowed to run into the bottle A from the tube B, the air in

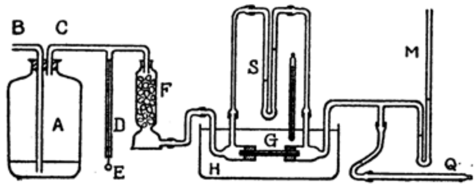

Fig. 3

A, being replaced by the water, will be expelled from the tube C under a certain pressure. The quantity of the air flowed out through the tube C could be controlled by regulating the water supply and by moving a copper wire E inserted in a capillary tube D. F is a drying tower filled with $CaCl_2$. G is a capillary flowmeter immersed in a thermostat H of 25°. S and M are manometers for measuring the pressure difference. Q is a quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. If a temperature elevation takes place at the capillary part of Q, then the velocity of the air stream which passes through the capillary will decrease. Consequently the pressure of the supplied air must be increased, in order to keep the quantity of the air allowed to pass through the capillary at a constant value. This increase of the pressure is read by the manometer M. Thus in carrying out the experiment, the temperature at the capillary part of the quartz tube Q and the pressure difference indicated by the manometer M should be read off, under the constant pressure difference of the manometer S. Potroleum of high boiling point was used for the manometer S and water for the manometer M. Two series of experiments have been performed, when the pressure difference indicated by the manometer S are 10 cm. and 20 cm. in petroleum column respectively. The adridged data are shown in Table 3. Taking log p and log T as coordinates, there is found a linear relation between them, as is shown in Fig. 4.

TABLE 3.

Press. diff. of flowmeter S, in cm. of petroleum.	Press. of air in cm. of water indicated by manometer M. (p)	log p	Abs. temp. (T)	log T	$p_{calc.}$	$T_{calc.}$
10	1.38	0.1399	290	2.4624	1.39	288
	2.52	0.4014	437	2.6405	2.52	437
	4.73	0.6749	675	2.8293	4.72	676
	7.37	0.8675	915	2.9614	7.33	918
	10.28	1.0120	1153	3.0618	10.24	1156
	14.42	1.1590	1478	3.1697	14.67	1461
20	3.92	0.5933	287	2.4579	3.96	285
	6.98	0.8439	439	2.6425	7.05	436
	10.12	1.0051	573	2.7582	10.12	573
	16.44	1.2159	828	2.9178	16.66	819
	26.28	1.4196	1160	3.0645	26.37	1157
	36.00	1.5563	1479	3.1700	36.67	1459

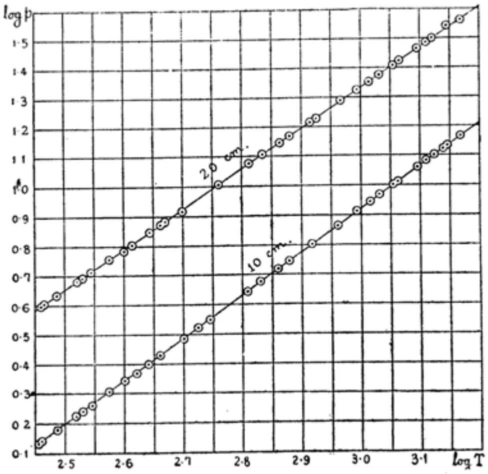

Fig. 4

Theoretical. In order to keep the quantity of the gas passing in a given interval through the quartz capillary always constant, notwithstanding the temperature of the capillary is elevated, the pressure of the gas must be increased. If we assume that all other conditions are constant, the gas must be compressed to its initial volume in order that the quantity of the transpirated gas should be kept invariably, and the pressure must change proportional to the absolute temperature, $p \propto T$. When the temperature is elevated, however, there takes place in the gas not only the increase of volume but also the increase of viscosity, so that the pressure must be increased a little more on account of the increase of viscosity. Let η be the viscosity, then we have

$$p \propto \eta, \quad \cdots\cdots\cdots\cdots(8)$$

therefore

$$\left.\begin{aligned} & p \propto \eta T, \\ & \frac{p}{p_0} = \frac{\eta T}{\eta_0 T_0} \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots(9)$$

or

According to Sutherland the relation between the viscosity and the absolute temperature T may be expressed by the following equation.

$$\frac{\eta}{\eta_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{2}} \frac{1+\dfrac{c}{T_0}}{1+\dfrac{c}{T}} \cdots\cdots\cdots\cdots(10)$$

so

$$p = p_0\left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{1+\dfrac{c}{T_0}}{1+\dfrac{c}{T}} \cdots\cdots\cdots\cdots(11)$$

or

$$p = kT^{\frac{3}{2}}\left(1+\frac{c}{T}\right)^{-1} \cdots\cdots\cdots\cdots(12)$$

If c is small, and T is large in equation (12), we may put

$$\log p = \log k + \tfrac{3}{2} \log T \cdots\cdots\cdots\cdots(13)$$

This shows that the relation between log p and log T is linear, agreeing with the results shown in Fig. 4. Assuming a more general form,

$$\log p = a \log T + b \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14)$$

two constants a and b being calculated by the method of least square from the observed data, thus:

Press. diff. on manometer S=10 cm., $a=1.4462$, $b=-3.4176$.

Press. diff. on manometer S=20 cm., $a=1.3582$, $b=-2.7414$.

In equation (13) which is derived from Sutherland's formula, the constant a is $\frac{3}{2}$. According to the above results, the value of a is smaller than $\frac{3}{2}$, but not very different from it. The values of the pressure p calculated by applying the above values of a and b in equation (14) are shown in the sixth column of Table 3. The calculated values are in good agreement with the observed values.

For the determination of temperature by measuring the pressure of gases, equation (14) must be transformed into the following form.

$$\log T = a' \log p + b' \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

The values of a' and b' are found as follows.

Press. diff. on manometer S=10 cm., $a'=0.69146$, $b'=2.3632$.

Press. diff. on manometer S=20 cm., $a'=0.73623$, $b'=2.0183$.

The values of the temperature ($T_{\text{calc.}}$), corresponding to the observed p, calculated from equation (15) are shown in the seventh column of Table 3. Comparing the calculated values with observed values of T, we see that this method may be used for the determination of high temperatures with equally good result as other pyrometers.

It was thus shown that this method is applicable from common temperature up to about 1200°C. For lower temperatures experiments have not yet been undertaken. Assuming that the equation (12) could be applied also in this case, the linear equation (13) hardly be employed, as the factor $1+c/T$ becomes greater. The curve representing the required relation should deviate from the straight line which represents equation (13), as the temperature falls. As to the method of experiment, the apparatus shown in Fig. 3 can be employed without any alterlation for lower temperatures. At much lower temperatures, however, the pressure difference in the manometer M will be so small that the readings becomes very difficult. For this reason it will be better to modify the method of measurement, namely, to exchange the rôle of two manometers, and the difference in S should be read off, the difference in M being maintained to be constant, as the difference in S becomes greater according as the temperature falls.

Summary.

Three methods have been studied for the purpose of determining high temperature by the observation of the rate of flow of gas. In the first method the temperature is determined by the effusion of gas, time necessary for the escape of a definite quantity of gas being observed. The following equation can be applied for the range from the common temperature up to about 1000°,

$$t=a+b\sqrt{T}\ ,$$

where T is the temperature, t is the time of effusion of air which passes through a quartz opening, and a and b are constants. This method might be useful, as the apparatus employed for this purpose is very simple and the relation between time and temperature can be represented by a simple equation.

In the second method, the temperature is measured by the transpiration of gases through a quartz capillary, the time of flow being measured also in this case. In the range from common temperature up to about 1000°, the logarithms of the absolute temperature can be expressed as an equation of second order of the logarithms of the time.

In the third method, the increase of the pressure necessary to maintain a constant rate of flow was observed. In the range from the common temperature up to about 1200°, there was found a linear relation between the logarithm of pressure and that of absolute temperature.

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Chemical Institute, Faculty of Science,
Tokyo Imperial University.