On the Flow of Gases through a Porous Wall.

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The rate of flow of gases through a porous plate was studied by Sameshima[(1)] and the following formula was introduced empirically by him.

$$t = k\eta^n M^{\frac{1-n}{2}},$$

where t is the time of flow of a definite volume of the gas, η the viscosity, M the molecular weight of the gas, k and n are constants independent of the kind of the gas but dependent on the nature of the porous plate and the pressure of the gas.

It was reported by the present author[(2)] that, when a gas flows through a capillary, the quantity flowing in unit time is expressed by the following formula:

$$Q = K(p_1 - p_2)$$

$$\text{or} \qquad K = A\frac{r^4}{l}p + \gamma B\frac{r^3}{l} \quad (\text{in mm.} \times \text{c.c.}), \tag{1}$$

$$\text{where} \qquad A = 5.236 \times 10^2 \frac{1}{\eta}, \qquad B = 3.05 \times 10^4 \sqrt{\frac{T}{M}},$$

K is the quantity of flow for unit pressure difference, measured by the product of the pressure and the volume, l and r the length and the radius of the capillary, p_1 and p_2 the pressures (measured in mm.) at the ends of the capillary, p the mean of these, T the temperature and γ a coefficient depending on pressure. This formula holds generally over a wide range of pressure, namely for various values of the ratios of the mean free path of the gas and the diameter of the capillary.

A porous plate may be considered to be composed of numerous pores of various diameters. If the diameters of all pores are large against the mean free path, the part of the molecular flow becomes negligible, and if the diameters are small against the mean free path, pure molecular flow will take place. However, in the case of an actual porous plate, the

(1) J. Sameshima, this Bulletin, **1** (1926), 5.
(2) This Bulletin, **12** (1937), 292.

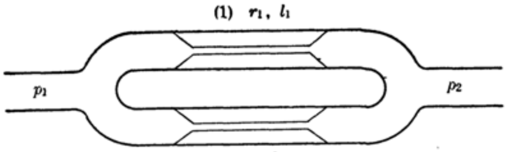
diameters of some pores may be large while those of others small against the mean free path.

Therefore, by using equation (1) we will be able to derive the formula of flow through a porous plate of any kind.

Flowing Formula of a Gas through a Porous Plate. We assume, before everything, that all pores of a porous plate are parallel and each pore may not have an uniform diameter but be composed of short pores of various diameters.

In order to know the flowing formula of a gas through a porous plate, we will treat, in the first place, the simple cases of the flow through many capillaries, whose radii and state of connection are known.

(i) **Flowing formula of a gas through numerous capillaries, which are connected in parallel.** When two capillaries, whose radii and lengths



are r_1, r_2 and l_1, l_2, are connected in parallel, the quantity flowing through capillary (1) in unit time and under unit pressure difference is given by

$$K_1 = A\frac{r_1^4}{l_1}p + \gamma B\frac{r_1^3}{l_1},$$

and the quantity through capillary (2) by

$$K_2 = A\frac{r_2^4}{l_2}p + \gamma B\frac{r_2^3}{l_2},$$

then the total quantity, K', becomes

$$K' = K_1 + K_2 = A\left(\frac{r_1^4}{l_1} + \frac{r_2^4}{l_2}\right)p + \gamma B\left(\frac{r_1^3}{l_1} + \frac{r_2^3}{l_2}\right).$$

The validity of this equation was examined numerically by measuring the quantities of hydrogen through the following capillaries:

Capillary (1): $r_1 = 0.0121$ cm., $l_1 \doteqdot 8.7$ cm.,

,, (2): $r_2 = 0.0073$ cm., $l_2 \doteqdot 8.8$ cm.

The values of K_1, K_2, and K' are given in Table 1. In this table, for the convenience of comparison, the values of three kinds of K are obtained respectively by the interpolation for the same pressures.

Table 1.

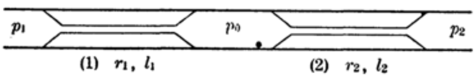
$p_{mm.}$	K_1	K_2	K_1+K_2	$K'_{obs.}$
3.0	0.1103	0.0181	0.1286	0.1285
2.0	0.0960	0.0170	0.1130	0.1132
1.0	0.0822	0.0160	0.0982	0.0980
0.8	0.0795	0.0154	0.0949	0.0950
0.6	0.0766	0.0150	0.0916	0.0917
0.4	0.0742	0.0147	0.0889	0.0889
0.2	0.0730	0.0144	0.0874	0.0865
0.1	0.0737	0.0155	0.0892	0.0890
0.05	0.0745	0.0164	0.0909	0.0905

As seen from Table 1, the observed values of K' agree very well with those calculated by the equation. Hence, when numerous capillaries, whose radii and lengths are $r_1, r_2, r_3, \ldots\ldots r_n$, and $l_1, l_2, l_3, \ldots\ldots l_n$, are connected in parallel, the quantity of flow is expressed by

$$K' = A\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}+\frac{r_3^4}{l_3}+\cdots\right)p+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}+\frac{r_3^3}{l_3}+\cdots\right)$$

$$= Ap\sum^{n}\frac{r_i^4}{l_i}+\gamma B\sum^{n}\frac{r_i^3}{l_i} . \qquad (2)$$

(ii) **Flowing formula through numerous capillaries, which are connected in series.** When two capillaries are connected in series, we



denote the pressure between the capillaries as p_0. The quantity flowing through capillary (1) in unit time is given by

$$Q_1 = A\frac{r_1^4}{l_1}\,\frac{p_1+p_0}{2}(p_1-p_0)+\gamma B\frac{r_1^3}{l_1}(p_1-p_0) ,$$

and that through capillary (2) by

$$Q_2 = A\frac{r_2^4}{l_2}\,\frac{p_0+p_2}{2}(p_0-p_2)+\gamma B\frac{r_2^3}{l_2}(p_0-p_2) .$$

As these two quantities are equal, then

$$Q'' = K''(p_1-p_2) = Q_1 = Q_2 ,$$

where K'' is the quantity flowing in unit time and under unit pressure difference through two capillaries connected in series,

From these three formulæ

$$\frac{1}{K''}=\frac{1}{K_1+A\frac{r_1^4}{l_1}\frac{p_0-p_2}{2}}+\frac{1}{K_2-A\frac{r_2^4}{l_2}\frac{p_1-p_0}{2}},$$

where K_1 and K_2 are the quantities flowing through capillaries (1) and (2) respectively, when each of them is alone.

Thus when two capillaries are connected in series, $1/K''$ is not equal to $(1/K_1+1/K_2)$.

By eliminating p_0, $1/K''$ is also written in the form

$$\frac{1}{K''}=\frac{1}{K_1}+\frac{1}{K_2}+\Delta_1,$$

where $$\Delta_1=\frac{(c_2d_1-c_1d_2)/c_1}{K_1K_2}\cdot\frac{1}{1+\frac{2K_1(c_1+c_2)/c_1}{(c_1+c_2)-(K_1+K_2)+\sqrt{\{(K_1-K_2)+(c_1+c_2)\}^2+4K_1K_2}}}$$

$$c_1=\frac{1}{2}A\frac{r_1^4}{l_1},\quad c_2=\frac{1}{2}A\frac{r_2^4}{l_2},\quad d_1=\gamma B\frac{r_1^3}{l_1},\quad d_2=\gamma B\frac{r_2^3}{l_2}.$$

The value of Δ_1 is estimated, by inserting numerical values, to be so small that it affects the value of K'' only less than 1%. Then, by neglecting Δ_1

$$K''=\frac{1}{\frac{1}{K_1}+\frac{1}{K_2}}=Ap\frac{1}{\frac{l_1}{r_1^4}+\frac{l_2}{r_2^4}}+\gamma B\frac{1}{\frac{l_1}{r_1^3}+\frac{l_2}{r_2^3}}+\Delta_2,$$

where $$\Delta_2=\frac{Ap\cdot\gamma B\dfrac{\left(\frac{r_1^3}{l_1}\frac{r_2^3}{l_2}\right)^2(r_1-r_2)^2}{\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}\right)\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}\right)}}{Ap\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}\right)+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}\right)}.$$

Δ_2 is also found under ordinary experimental conditions to have a value smaller than 1% of the other terms. Then we have

$$K''=Ap\frac{1}{\frac{l_1}{r_1^4}+\frac{l_2}{r_2^4}}+\gamma B\frac{1}{\frac{l_1}{r_1^3}+\frac{l_2}{r_2^3}}.$$

Table 2.

$p_{\text{mm.}}$	K'' obs.	K'' calc.
3.0	0.0159	0.0165
2.0	0.0144	0.0148
1.0	0.0130	0.0133
0.5	0.0199	0.0123
0.1	0.0128	0.0128
0.05	0.0129	0.0129

This equation was examined numerically by using the two capillaries described above. (Table 2.)

It will be seen from the table, that the results are satisfactorily expressed by the above equation justifies the neglections made in obtaining it.

When numerous capillaries are connected in series, the quantity of flow is expressed by

$$K'' = A\frac{1}{\sum\limits^{m}\frac{l_i}{r_i^4}}p+\gamma B\frac{1}{\sum\limits^{m}\frac{l_i}{r_i^3}}\,. \tag{3}$$

As it was assumed, if all pores of a porous plate are parallel and each pore is composed of series of short pores having various diameters, the quantity of a gas flowing through a porous plate can be expressed by the combination of equations (2) and (3) as follows:

$$K = Ap\sum^{n}\frac{1}{\sum\limits^{m}\frac{l_i}{r_i^4}}+\gamma B\sum^{n}\frac{1}{\sum\limits^{m}\frac{l_i}{r_i^3}}\,,$$

or $K = ApE+\gamma BF$

$$= 5.236\times 10^2\frac{1}{\eta}Ep+2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in mm.}\times\text{c.c.)}, \tag{4_1}$$

where $E=\sum\frac{1}{\sum\frac{l_i}{r_i^4}}$, $F=\sum\frac{1}{\sum\frac{l_i}{r_i^3}}$, and γ is taken as 0.9. E and F are functions of the radii and lengths of pores. The actual construction of pores is so complicated that the functional forms of these coefficients can not be obtained directly. If pressures are measured in atmospheric unit, the above equation becomes

$$K = 3.979\times 10^5\frac{1}{\eta}Ep+2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in atm.}\times\text{c.c.)}. \tag{4_2}$$

Equation (4) was examined numerically by measuring the quantities of flow through a few kinds of porous plates. As an example, the results of comparison between the values observed by Sameshima[(1)] and those of calculated by (4) are given in Table 3. Sameshima measured the time of flow of a definite volume (ca. 70 c.c.) of seven gases at the following pressures: $p_1 = 1.0$, 1.5, 2.0, 2.5 atm.; $p_2 = 0$; so that $p = 0.5$, 0.75, 1.0, 1.25 atm. By the method of least square, the values of two constants E and F were obtained as follows: $E = 1.83 \times 10^{-11}$, $F = 3.45 \times 10^{-7}$. Hence the flowing formula of a gas at 25°C. through the porous plate (an unglazed earthen-ware) used by Sameshima becomes

$$K = 7.282 \times 10^{-6} \frac{1}{\eta} p + 1.636 \times 10^{-1} \frac{1}{\sqrt{M}} \quad \text{(in atm.} \times \text{c.c.).}$$

This formula was used for the calculation of the values of K given in Table 3.

Table 3. The Quantities of Flow of Gases through the Porous Plate observed by Sameshima.

$p_{atm.}$	0.5		0.75	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.0728	0.0735	0.0892	0.0898
NH_3	0.0742	0.0747	0.0919	0.0922
C_2H_2	0.0668	0.0672	0.0844	0.0847
C_2H_4	0.0648	0.0669	0.0825	0.0849
Air	0.0495	0.0504	0.0600	0.0603
O_2	0.0460	0.0465	0 0552	0.0552
CO_2	0.0480	0.0482	0.0602	0.0600
$p_{atm.}$	1.0		1.25	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.1054	0.1061	0.1220	0.1224
NH_3	0.1098	0.1096	0.1276	0.1282
C_2H_2	0.1021	0.1023	0.1200	0.1198
C_2H_4	0.1000	0.1029	0.1167	0.1209
Air	0.0698	0.0702	0.0798	0.0802
O_2	0.0642	0.0640	0.0732	0.0727
CO_2	0.0724	0.0717	0.0844	0.0834

As seen from Table 3, the quantity of a gas flowing through the porous plate is expressed satisfactorily by equation (4).

The present author with M. Tachimori measured also the quantities of flow through a few kinds of porous plates and found that the quantities

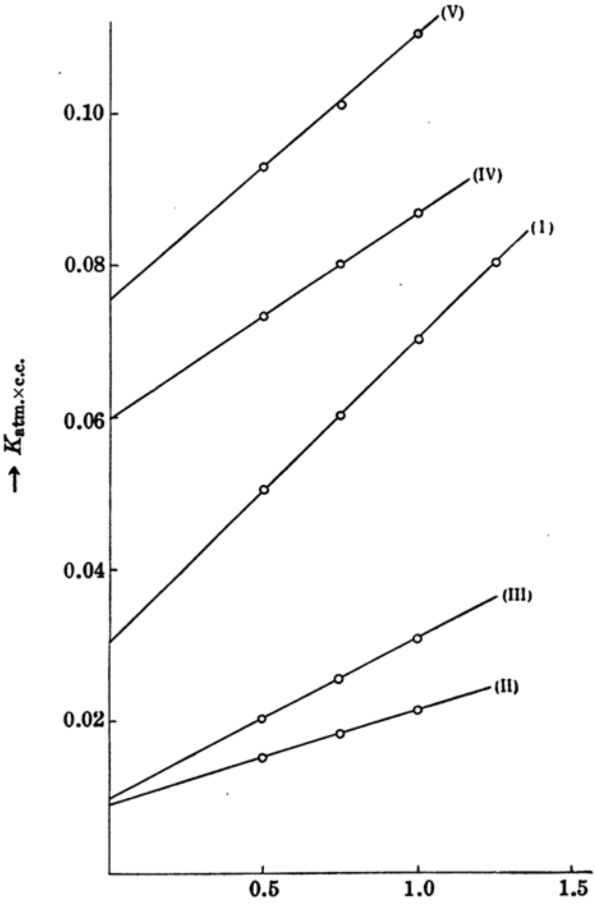


Fig. 1. Quantities of Air Flowing through Porous Plates.

are also expressed by equation (4). The results are represented graphically in Fig. 1.

The values of E and F for the several porous plates and gases used for experiments are tabulated in Table 4.

Table 4.

	Porous plate	Gas	Temp.	$E\times10^{11}$	$F\times10^{7}$
(I)	Unglazed earthen-ware used by Sameshima	CH_4, etc.	25°C.	1.83	3.45
(II)	Porous plate used in organic preparation (compact)	Air	20	0.45	1.64
(III)	,, (rough)	Air	20	0.83	1.72
(IV)	Mantle of a Daniell cell (white)	Air	25	1.1	6.82
(V)	,, (red)	Air	25	1.5	8.58

Mean Radius and Number of Pores per unit Area of a Porous Matter. For many purpose it is sufficient to know the mean value of the pore radii of porous matters, for example unglazed earthen-wares, glass-filters, filterpapers, membranes of colloidon, etc. As already pointed out, the construction of pores of a porous matter is so complicated that we can not find any method to obtain the actual radius and number of pores. Therefore, in order to estimate the radius, we must take some simplifications about the construction of pores. The simplest assumption is that each pore has an uniform radius. Several methods of obtaining the radius, under this assumption, have been introduced. Bartell and Osterhof(3), and Uehara(4) obtained the radii of porous matters by measuring the pressure necessary to prevent ascension of a liquid in the capillaries and Anderson(5) by measuring the change of the vapour pressure in the capillaries. Kawakami(6) estimated them from the measurements of the quantity of effusion, the electric conductivity, and the maximum linear velocity of a liquid in a porous matter.

If all pores of the porous plate have the uniform radius, R, and are normal to the surface, E and F can be written in a very simple form as follows:

$$E = nR^4/d\,, \qquad F = nR^3/d\,,$$

where n is the number of pores and d the thickness of the porous plate. Hence, E and F are proportional to the area of the surface and inversely proportional to the thickness of the plate, so that the values for unit area

(3) F. E. Bartell and H. J. Osterhof, *J. Phys. Chem.*, **32** (1928), 1553.
(4) K. Uehara, *J. Chem. Soc. Japan*, **55** (1934), 75.
(5) J. S. Anderson, *Z. physik. Chem.*, **88** (1914), 191.
(6) M. Kawakami, *J. Chem. Soc. Japan*, **53** (1932), 1085; **54** (1933), 133.

and unit thickness, E_0, F_0, can be easily obtained by $E_0 = Ed/\text{area}$, $F_0 = Fd/\text{area}$.
Then we have

$$E_0 = NR^4 \quad \text{and} \quad F_0 = NR^3 ,$$

where N is the number of pores per unit area of the surface.
From these formulæ,

$$R = E_0/F_0 , \qquad N = F_0^4/E_0^3 . \tag{5}$$

The values of R and N for several porous plates calculated by equation (5) are given in Table 5.

Table 5. Mean Diameters of Pores and Number of Pores per Unit Area.

Porous plate	Thickness	Area	$E_0\times10^{11}$	$F_0\times10^{7}$	$R\times10^{5}$ cm.	N
(I)	0.15 cm.	0.28 cm.^{2}	0.97	1.83	5.3	1.2×10^{6}
(II)	0.27	2.22	0.054	0.195	2.77	2.4×10^{5}
(III)	0.41	2.22	0.154	0.318	4.84	2.8 ,,
(IV)	0.2	0.27	0.80	4.98	1.61	0.96×10^{8}
(V)	0.2	0.27	1.09	6.26	1.74	1.19 ,,

Summary.

(1) A formula for the flow of a gas through a porous plate has been derived and found that the observed quantity of flow is satisfactorily expressed by this formula.

(2) The method of estimating the values of the mean radius and the number of pores of a porous plate has been proposed.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

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