The Flow of Gases through Metallic Capillaries at Low Pressures.

By Hiroshi ADZUMI.

(Received August 5, 1939.)

It was reported by the present author⁽¹⁾ that the quantity of a gas flowing through a capillary in unit time and under unit pressure difference is expressed by the following formula:

$$K = 5.236 \times 10^2 \frac{1}{\eta} \frac{r^4}{l} p + \gamma \times 3.05 \times 10^4 \sqrt{\frac{T}{M}} \cdot \frac{r^3}{l}, \quad \ldots\ldots \ (1)$$

where η is the viscosity coefficient of the gas, M the molecular weight, p the mean pressure in mm. Hg, T the temperature, l and r respectively the length and the radius of the capillary and γ a coefficient equal to or smaller than unity. The flowing quantity K is measured by the product of the volume and the pressure of the gas. Coefficient γ of a gas is a function of pressure, but is constant at very low pressures, where it is equal to unity, and also constant at high pressures, where it is equal to about 0.9. This constant value of γ at high pressures is slightly different from gas to gas.

---

(1) H. Adzumi, this Bulletin, **12** (1937), 292.

An interesting phenomenon about the flow of gases at low pressures is the existence of a minimum point on the K-p curve. The theoretical interpretation of it has not yet been done, but if the nature of γ be cleared, the existence of a minimum will probably be explained. As stated above, γ is a coefficient depending on the nature of gases, but it is not known whether it depends on the nature of the capillary-wall or not. Almost all capillaries which were used by many authors to study the flowing phenomena of gases were made of glass. In order to know the effect of the material of the capillary-wall, the present experiments have been done.

Experimental. The procedure for measuring the quantities of flow of gases is the same as already described.⁽²⁾ The material of capillaries used for experiments are glass, silver, aluminium, copper, and iron. The inner surfaces of these metallic capillaries were carefully made as smooth as possible. The internal diameters are about 0.054 ~ 0.058 cm. and lengths 5 ~ 10 cm. The exact dimensions of respective capillaries are shown in the accompanying tables. The quantities of hydrogen flowing in unit time and under unit pressure difference through various metallic capillaries at 15.5°C. are given in Table 1.

As the reproducibility of the quantities at pressures lower than about 0.05 mm. Hg was not good, the values of extremely low pressures are

Table 1. The Quantities of Flow of Hydrogen at 15.5°C.

Capillary: silver

(l = 7.7 cm., r = 0.027 cm.)

$p_{\text{mm.}}$	K	$K-ap$	γ	
1.517	1.456	0.844	0.89	0.89
1.210	1.329	0.841	0.89	
1.109	1.290	0.846	0.90	
0.8258	1.176	0.843	0.89	
0.5850	1.080	0.844	0.89	
0.5612	1.068	0.842	0.89	
0.4022	1.004	0.842	0.89	
0.2995	0.975	0.844	0.89	
0.2229	0.952	0.862	0.91	
0.1821	0.944	0.871	0.92	
0.1646	0.941	0.874	0.92	
0.1375	0.941	0.886	0.94	
0.1018	0.939	0.898	0.95	
0.0677	0.936	0.909	0.96	
0.0578	0.937	0.914	0.97	
0.0436	0.940	0.922	0.98	
0.0329	0.939	0.926	0.98	
(0.000)	(0.945)	0.945	1.00	

Capillary: aluminium

(l = 5.4 cm., r = 0.029 cm.)

$p_{\text{mm.}}$	K	$K-ap$	γ	
1.421	2.490	1.378	0.81	0.81
1.388	2.464	1.378	0.81	
0.8951	2.073	1.372	0.81	
0.8188	2.017	1.376	0.81	
0.5431	1.801	1.376	0.81	
0.4985	1.765	1.374	0.81	
0.3434	1.655	1.387	0.82	
0.3173	1.642	1.394	0.82	
0.2217	1.590	1.416	0.83	
0.2040	1.585	1.427	0.84	
0.1449	1.567	1.454	0.86	
0.1347	1.560	1.455	0.86	
0.1156	1.560	1.469	0.87	
0.1000	1.558	1.480	0.87	
0.0718	1.561	1.505	0.89	
0.0387	1.574	1.544	0.91	
0.0237	1.588	1.569	0.92	
0.0202	1.594	1.578	0.93	
(0.000)	(1.699)	1.699	1.00	

---

(2) H. Adzumi, this Bulletin, **12** (1937), 285.

Capillary: copper

($l = 9.8$ cm., $r = 0.030$ cm.)

$p_{mm.}$	K	$K-ap$	γ	
1.604	1.483	0.764	0.79	0.79
1.444	1.408	0.761	0.79	
1.063	1.241	0.766	0.80	
0.9690	1.192	0.758	0.79	
0.7365	1.092	0.762	0.79	
0.6801	1.065	0.760	0.79	
0.5265	1.001	0.765	0.79	
0.3230	0.914	0.769	0.80	
0.2225	0.885	0.785	0.82	
0.2181	0.888	0.790	0.82	
0.1350	0.872	0.811	0.84	
0.1175	0.870	0.817	0.85	
0.0744	0.875	0.842	0.87	
0.0645	0.876	0.847	0.88	
0.0378	0.886	0.869	0.90	
0.0376	0.892	0.875	0.91	
0.0290	0.893	0.880	0.91	
0.0185	0.901	0.893	0.93	
(0.000)	(0.963)	0.963	1.00	

Capillary: iron

($l = 9.96$ cm., $r = 0.029$ cm.)

$p_{mm.}$	K	$K-ap$	γ	
2.073	1.412	0.626	0.74	0.73
1.462	1.176	0.622	0.73	
0.9332	0.971	0.617	0.73	
0.6889	0.880	0.618	0.73	
0.5291	0.821	0.620	0.73	
0.4039	0.785	0.632	0.75	
0.3951	0.784	0.634	0.75	
0.3036	0.762	0.647	0.76	
0.2815	0.755	0.648	0.77	
0.2371	0.752	0.662	0.78	
0.1864	0.739	0.668	0.79	
0.1643	0.737	0.675	0.80	
0.1464	0.738	0.683	0.81	
0.0914	0.736	0.701	0.83	
0.0720	0.737	0.710	0.84	
0.0574	0.740	0.718	0.85	
0.0440	0.744	0.727	0.86	
0.0395	0.750	0.735	0.87	
(0.000)	(0.846)	0.846	1.00	

obtained by calculation from formula (1) and are shown in brackets in the tables. The symbol ap in the third column of the tables indicates the first term of formula (1). In Fig. 1, K's are shown as functions of the mean pressures. These figures are similar to that in the case of capillary of glass and the existence of minimum points is also remarkable. As seen from the fourth columns of the tables, γ's for various capillaries become respectively constant at high pressures. These constant values, which are denoted by γ_m, are shown in Table 2 in comparison with the value for the glass capillary.⁽¹⁾

As seen from Table 2, the values of γ_m clearly depend upon the material of the capillary-wall.

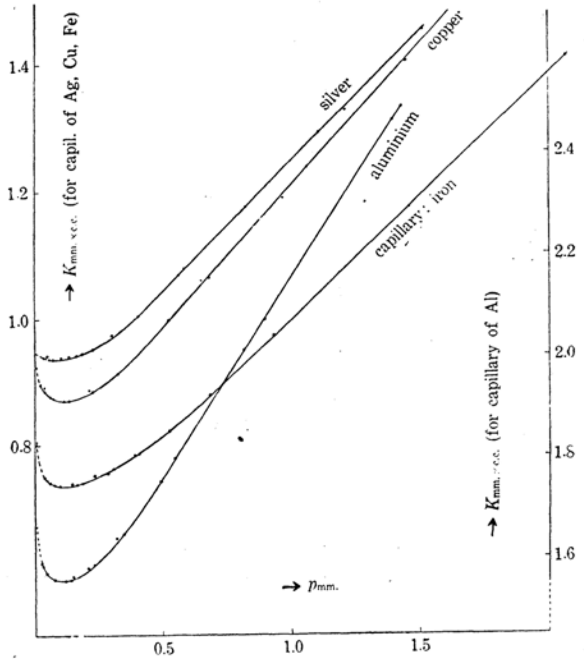

Fig. 1.

Table 2. Values of γ_m for Various Capillaries.

Capillaries	Glass	Silver	Aluminium	Copper	Iron
γ_m	0.91	0.89	0.81	0.79	0.73

Discussion. As stated above, the theoretical interpretation of the existence of a minimum point on the K-p curve has not yet been done. Considering the dependence of γ_m upon the material of the capillary-wall and upon the flowing gas, the author advances the following argument. At very low pressures there are no molecules adsorbed on the surface of the capillary-wall but on increasing the pressure the adsorption will take place and the adsorbing area will be increased. At high pressures the surface will be saturated. Let us now consider the intermediate pressures at which the surface is not saturated. It is assumed that all the molecules which fall on the bare surface are adsorbed and that only some fraction of the molecules which fall on the already adsorbed molecules are reflected immediately. If this fraction of the reflected molecules is denoted by β, then $1-\beta$ is the fraction of molecules adsorbed. Therefore, of all the impinging molecules on the capillary-surface a fraction ρ will be adsorbed and this fraction is expressed as

$$\rho = \theta(1-\beta)+(1-\theta)\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where θ is the fraction of the surface area already occupied, so that $1-\theta$ is that of the bare surface. When the surface is not saturated, the fraction θ depends on the pressure, and this will increase only when molecules fall on the bare surface $(1-\theta)$. Therefore, $d\theta/dp$ is considered to be proportional to $1-\theta$, then

$$\frac{d\theta}{dp} = c(1-\theta),$$

where c is the proportionality constant. By integration

$$\theta = 1-e^{-cp}\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

the integration constant being zero.
From (2) and (3),

$$\rho = 1-\beta(1-e^{-cp})\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If only a fraction f of the impinging molecules leave the wall according to the cosine law (this is called 'diffuse emission') and the remainder, $1-f$, are regularly reflected, some factor must be introduced into the formula of the molecular flow. This factor was given as $f/(2-f)$ by Gaede.⁽³⁾

Of all the impinging molecules, the adsorbed ones will be emitted after some stay in the adsorption layer, independently to the incident angle. So that the fraction of the diffuse emission (f) is exactly equal to the fraction of adsorption (ρ). Hence, by introducing the value of ρ to f, γ is expressed as follows:

---

(3) W. Gaede, *Ann. Physk*, (IV), **41** (1913), 289.

$$\gamma = \frac{f}{2-f} = \frac{1-\beta(1-e^{-cp})}{1+\beta(1-e^{-cp})}\ .$$

Thus the relation between γ and pressure is derived. At high pressures γ becomes constant, $(1-\beta)/(1+\beta)$, and at very low pressures it becomes approximately unity. At intermediate pressures γ depends on the pressure. This formula contains two unknown constants, β and c. In Table 3 are shown these constants calculated inversely from the observed data.

Table 3. Values of β and c for Hydrogen.

Capillaries	Silver	Aluminium	Copper	Iron
β	0.058	0.104	0.117	0.156
c	6.9	10.1	10.2	7.5

By using these calculated constants the flowing quantities K can be computed and these coincide satisfactorily with the experimental values. For example, the coincidence of these values of K's in the case of iron capillary is indicated in Table 4 and Fig. 2.

Table 4.
Values of K calculated.
(Capillary: iron)

$p_{\text{mm.}}$	$K_{\text{obs.}}$	$K_{\text{calc.}}$
1.0	0.998	0.997
1.7	0.884	0.883
0.5	0.813	0.812
0.3	0.760	0.766
0.2	0.744	0.739
0.1	0.736	0.733
0.05	0.742	0.779

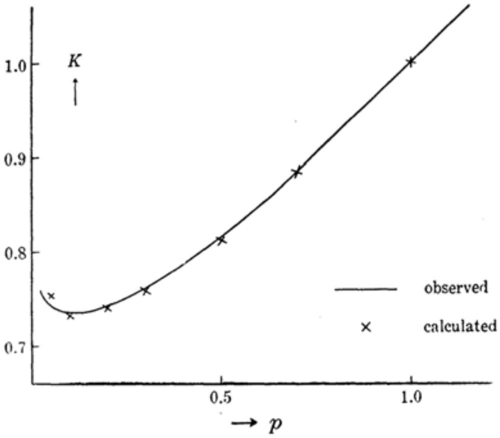

Fig. 2.

To summarize the preceding considerations, it can be said that, notwithstanding that the derived formula contains two unknown constants, the existence of a minimum point on the K-p curve and the character of the factor γ in the flowing formula have been qualitatively interpreted.

In conclusion, the author wishes to express his cordial thanks to Professor Emeritus M. Katayama and Prof. H. Tominaga for their encouragement throughout this experiment. Thanks are due to the Japan Society for the Promotion of Scientific Research for a grant.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.