Studies on the Flow of Gaseous Mixtures through Capillaries. II. The Molecular Flow of Gaseous Mixtures.

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In the preceding paper⑴ on the flow of gaseous mixtures, the author dealt with the case where the mean free path of the gas molecule of each component is small in comparison with the diameter of the capillary. When the mean free path is large in comparison with the diameter, the number of mutual collisions between gas molecules is negligible as compared with that of collisions with the wall. In such a case, Knudsen⑵ has assumed "the diffuse emission" from the wall of the capillary, namely, the molecules in the capillary leave a surface uniformly in all directions regardless of the directional distribution with which they hit the surface and are governed by the cosine law. As a result of this behaviour some of the molecules entering the mouth of the capillary are reversed and sent back to the vessel from which they came. Hence the number of molecules flowing through the capillary is a certain fraction of the total number of entering molecules and this fraction is determined only by the number of collisions with the wall of the capillary and not by the collisions between molecules.

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(1) H. Adzumi, this Bulletin, **12** (1932), 199.

(2) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.

When the mean free path is large against the diameter of the capillary, the quantity of a simple gas flowing through the capillary in unit time is given by Knudsen as follows:

$$G_m = b(p_1 - p_2)\ , \tag{1}$$

where

$$b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{r^3}{l}\ ,$$

ρ_1 is the density of the gas at the temperature of the capillary and at unit pressure (1 dyne/cm.^{2}), l and r are the length and the radius of the capillary respectively, p_1 and p_2 the pressures at the ends of the capillary, and G_m is measured by the product of its volume and pressure. Thus the amount of gas flowing per unit time is independent of the viscosity but inversely proportional to the square root of the molecular weight and therefore such a flow is called the molecular flow.

In their theoretical considerations of the flow of gases Maxwell(3), Smoluchowski(4), Gaede(5), and Baule(6) made the assumption that only a fraction f of the impinging molecules leave the wall according to the cosine law and that the reflection for remaining 1-f are specular. However, from the experiments, Knudsen gave the value of f as unity.

In an ideal gaseous mixture, each component is completely independent of the other, since the molecules do not affect each other within the capillary. Therefore the amount of flow of a mixture will be strictly additive or

$$b = n_1 b_1 + n_2 b_2\ , \tag{2}$$

where n_1 and n_2 are mol fractions of two components.

In order to examine this point the following experiments have been done.

Experimental.

Apparatus for Measuring the Quantity of Flow. Fig. 1 is a schematic view of the apparatus. Glass bulbs A and B, both about 1 liter in capacity, are connected with the capillary C, whose radius is ca. 0.0121 cm. and length 8.7 cm. The pressure of each bulb is read by the McLeod gauge which is constructed to be able to measure from 10^{-5} to 10 mm. D and E are mercury cut-offs. When the mercury is raised to

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(3) J. Maxwell, *Trans. Roy. Soc.* (London), A, **170** (1879), 251.
(4) M. v. Smoluchowski, *Ann. Physik*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*, (IV), **41** (1913), 289.
(6) B. Baule, *ibid.*, (IV), **44** (1914), 145.

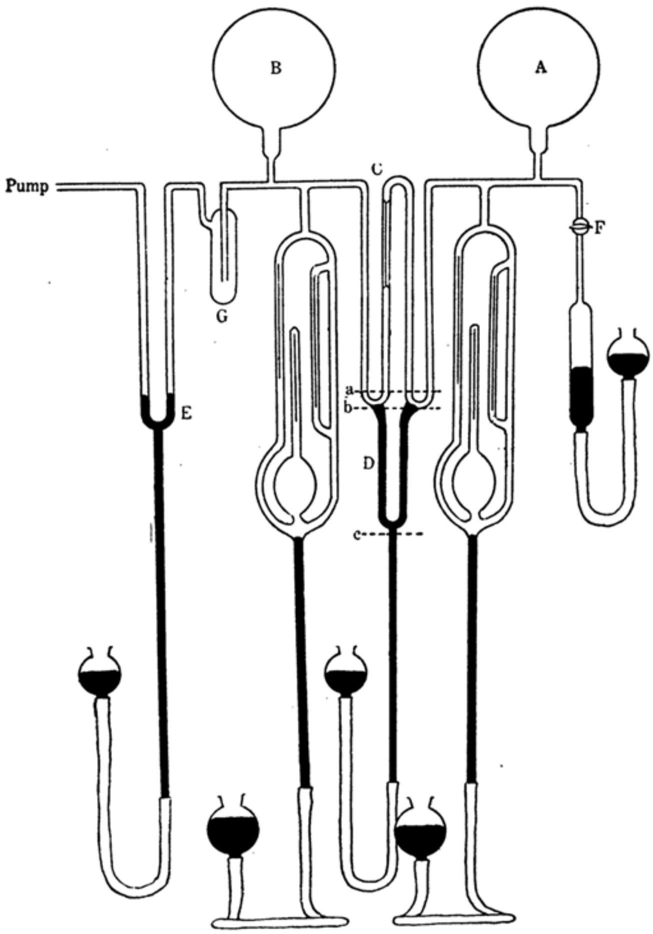

Fig. 1.

c, two bulbs are connected without the capillary, when raised to b, the gas flows through the capillary, and when raised to a, the flow is cut off.

After evacuation of the whole apparatus and raising the mercury to a, the required quantity of the gas is introduced into A from F. Then, by lowering the mercury to b, the gas in A begins to flow through the capillary, the volume on each side being kept constant.

If V_1 and p_1 represent the volume and the pressure of the right side of the capillary and V_2 and p_2 those of the left side, the quantity of gas flowing in time $d\tau$ through the capillary is expressed as

$$Q\cdot d\tau = K(p_1-p_2)\ d\tau = -d(p_1V_1) = d(p_2V_2)\ ,$$

where K is a proportionality constant or the quantity of flow under unit pressure difference, $-d(p_1V_1)$ a quantity decreased in the right side of the capillary, and $d(p_2V_2)$ a quantity increased in the left side.
Then,

$$\frac{K\cdot d\tau}{V_1} = -\frac{dp_1}{p_1-p_2} \quad \text{and} \quad \frac{K\cdot d\tau}{V_2} = \frac{dp_2}{p_1-p_2} ,$$

From these formulæ,

$$\frac{d(p_1-p_2)}{p_1-p_2} = -K\left(\frac{1}{V_1}+\frac{1}{V_2}\right)d\tau .$$

By integration

$$K = -\frac{\ln\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau}\,\frac{V_1\ V_2}{V_1+V_2} ,$$

where p_1' and p_2' are the pressures of bulbs after time $d\tau$. The values of V_1 and V_2 are 1371 c.c. and 1406 c.c. respectively, so that K is calculated by the following formula:

$$K = -\frac{\log\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau} \times 1.856 \times 10^3 \text{ (in mm.} \times \text{c.c.).}$$

The mean pressure of both ends of the capillary is calculated by

$$p = \frac{p_1V_1+p_2V_2}{V_1+V_2} .$$

Results of Observation. The gaseous mixtures used for observation are $H_2 \sim C_2H_2$ and $H_2 \sim C_3H_6$. The preparation of these gases was described in the preceding paper.(1) The measuring temperature was $20 + 0.5°C$. The pressure range was between 4 and 10^{-3}mm. The time of flow was 2–4 hours.

Generally the values of K are a function of the mean pressure p, but become a constant when p is so small that the mean free path of the gas is large against the diameter of the capillary. This constant value corresponds to the rate of the molecular flow, b. When the pressures of hydrogen, acetylene, and propylene are lower than 0.06 mm., 0.03 mm., and 0.03 mm. respectively, the values of K become constants, which are 0.0750 for H_2, 0.0220 for C_2H_2, and 0.0164 for C_3H_6.

The values of K at the pressures higher than those will be reported in the following paper.

Table 1. The Rates of the Molecular Flow of Simple Gases.

Gas	b (mm.×c.c.)	
	obs.	calc.
H_2	0.0750	0.0750
C_2H_2	0.0220	0.0208
C_3H_6	0.0164	0.0164

The rates of the molecular flow, b, of three simple gases can be calculated by equation (1), by inserting the following values: $l = 8.7$ cm., $r = 0.0121$ cm.; ρ_1 at 20°C. of $H_2 = 8.266 \times 10^{-11}$, $C_2H_2 = 107.88 \times 10^{-11}$, $C_3H_6 = 172.21 \times 10^{-11}$. These calculated values of b agree very well with the observed values of K at very low pressures. (Table 1.) This agreement shows that the fraction f of the molecules which leave the wall according to the cosine law is unity.

The values of K of a mixture, similarly as a simple gas, become a constant at very low pressures. In the cases of the flow of mixtures at low pressures, the compositions change every moment, since the quantities were measured at every thirty minutes and the quantities of flow of the initial compositions were obtained by extrapolating to time zero.

The values of b of mixtures are given in Table 2.

Table 2. The Rates of the Molecular Flow of Mixtures.

$H_2 \sim C_2H_2$

H_2%	C_2H_2%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.69	24.31	0.0622	0.0621
51.18	48.82	0.0490	0.0491
25.97	74.03	0.0354	0.0358
0.00	100.00	0.0220	0.0220

$H_2 \sim C_3H_6$

H_2%	C_3H_6%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.18	24.82	0.0610	0.0604
50.82	49.18	0.0458	0.0462
0.00	100.00	0.0164	0.0164

In Table 2, the values of b given in the fourth column are calculated by formula (2).

As seen from Table 2, the rates of molecular flow of gaseous mixtures strictly follows the additivity law.

The Separation of Mixtures caused by Flowing through Capillaries at Low Pressures. At very low pressures, each component of a mixture flows independently of the other, namely the separation of a mixture into components takes place. Consequently, by measuring the separation of the mixtures after flow, the additivity of the flowing quantity of mixtures may be confirmed.

In order to know the separation of the mixture $H_2 \sim C_2H_2$, the quantities of acetylene after flow were analysed by the following method: The trap G in Fig. 1 was cooled with liquid air and hydrogen was removed by vacuum pump, acetylene being condensed to solid state in G. Then acetylene in the trap was vaporised by removing the liquid air and its pressure was read. If the total pressure before the application of liquid air is known, the composition of the mixture after flow can be calculated. This analytical method has been examined beforehand by analysing the mixtures of known compositions and has been found that it can be used to know the composition within the experimental error of a few per cent.

The changes of the compositions of the mixtures after flowing through the capillary for two hours are given in Table 3.

Table 3. The Change of the Compositions after Flowing through the Capillary. (Fig. 2.)

Mixture I.

(H_2: 51.18%, C_2H_2: 48.82%)

$p_{mm.}$	H_2%	C_2H_2%
3.161	51.0	49.0
2.064	51.2	48.8
0.828	54.0	46.0
0.518	59.6	40.4
0.200	69.0	31.0
0.1471	72.0	28.0
0.0659	76.0	24.0
0.0493	75.8	24.2

Mixture II.

(H_2: 75.69%, C_2H_2: 24.31%)

$p_{mm.}$	H_2%	C_2H_2%
2.780	75.7	24.3
1.914	75.6	24.4
1.204	75.7	24.3
0.725	79.0	21.0
0.475	81.9	18.1
0.273	85.8	14.2
0.1453	88.0	12.0
0.0581	89.5	10.5

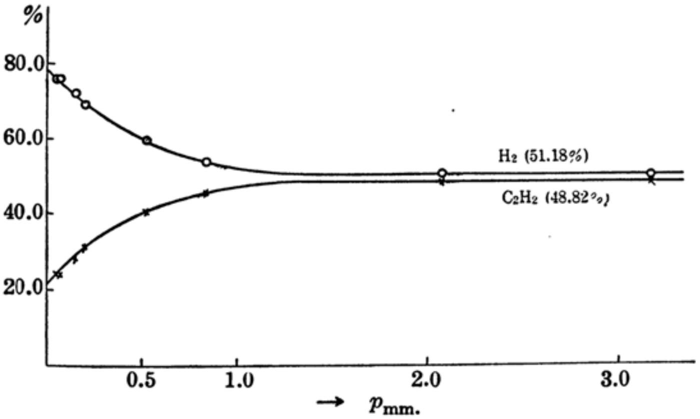

Fig. 2. The Change of the Compositions of Mix. I.

As seen from Fig. 2, the mixtures flow without separation at the pressures higher than about 1 mm. but at the pressures lower than this the separation takes place. By extrapolation of the curves to $p = 0$, the hydrogen percentages of the mixtures after flow at very low pressures can be obtained. These values are 78.5% for mixture I and 91.0% for mixture II and agree very well with the values which are calculated by considering that the component flows independently of the other. (Table 4.)

Table 4. The Hydrogen Percentages of the Mixtures after Flow at Very Low Pressures.

	H_2%	
	obs.	calc.
Mixture I	78.5	78.1
,, II	91.0	91.5

The same analytical method was applied to the mixture of hydrogen and propylene, but as the latter does not condense to solid state, there is an appreciable loss during the evacuation. Hence the reading of the pressure of propylene after evaporation was not accurate enough to compute the exact concentration.

Summary.

(1) The quantities of the following simple gases and gaseous mixtures flowing through the capillary at very low pressures have been measured.

$$H_2,\ C_2H_2,\ C_3H_6,\ H_2{\sim}C_2H_2,\ H_2{\sim}C_3H_6.$$

(2) The rates of the molecular flow of simple gases are expressed satisfactorily by Knudsen's formula.

(3) The rates of the molecular flow of mixtures are considered to be additive of the components. This consideration has been confirmed by the measurements of the quantities of flow of mixtures.

(4) The changes of the compositions of the mixtures after flowing through the capillary at low pressures have been measured and the results show also the validity of the additivity law.

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

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