Studies on the Flow of Gaseous Mixtures through Capillaries. III. The Flow of Gaseous Mixtures at Medium Pressures.

By Hiroshi ADZUMI.

(Received May 26th, 1937.)

In the previous papers⑴⑵, the author reported the studies on the flow of gaseous mixtures when the mean free paths of molecules are small or large in comparison with the diameter of the capillary. When the mean free path is small against the diameter, the quantity of a gas flowing in unit time is expressed by the following formula:

$$G_v = ap(p_1 - p_2)\,, \tag{1}$$

where

$$a = \frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l}\,,$$

η is the viscosity of the gas, p_1 and p_2 the pressures at the ends of the capillary, p the mean of these, and l and r are the length and the radius of the capillary. When the mean free path is large against the diameter, the quantity is expressed by

$$G_m = b(p_1 - p_2)\,, \tag{2}$$

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 unit pressure.

At medium pressures when the mean free path is comparable with the diameter, two above formulæ overlap each other and we may set as follows:

$$Q = G_v + \gamma G_m = K(p_1 - p_2)\,,$$

or

$$K = ap + \gamma b, \tag{3}$$

where γ is a coefficient which is equal to or smaller than unity.

In order to examine formula (3) for simple gases and binary gaseous mixtures, the following experiments have been done.

The Quantities of Flow of Simple Gases. The procedure for measuring the quantity of flow is the same as already described.⑵ The quanti-

---

(1) This Bulletin, **12** (1937), 199.
(2) *Ibid.*, **12** (1937), 285.

ties of hydrogen, acetylene, and propylene flowing in unit time and under unit pressure difference are given in Table 1. The mean pressures are measured in mm. In such a case, the formula of the quantity of flow becomes

$$K=\frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l}\frac{1013250}{760}p+\gamma\times3.05\times10^4\sqrt{\frac{T}{M}}\frac{r^3}{l}$$

$$=5.236\times10^2\frac{1}{\eta}\frac{r^4}{l}p+\gamma\times3.05\times10^4\sqrt{\frac{T}{M}}\frac{r^3}{l}, \qquad (4)$$

where M is the molecular weight of the gas and T the absolute temperature.

In Fig. 1, K is shown as function of the mean pressure. As seen from the figure, the observed values of K decrease with the decrease of the pressure, lying on a straight line at higher pressures, then after passing through a minimum, become a constant at very low pressures. As described in the preceding paper, this constant corresponds to the rate of the molecular flow. The shape of the curves in Fig. 1 shows that the flow can be expressed by formula (3).

The gradient a can be obtained from the straight part and by using it we can calculate the values of γ, which is shown in the fourth column

Table 1. The Quantities of Flow of Simple Gases. (Fig. 1.)

Hydrogen. (20°C.)

$p_{\text{mm.}}$	K	K-ap	γ	
2.811	0.1075	0.0680	0.91	0.91
1.869	0.0939	0.0677	0.90	
1.269	0.0858	0.0680	0.91	
0.893	0.0814	0.0689	0.92	
0.634	0.0769	0.0680	0.91	
0.526	0.0744	0.0670	0.89	
0.443	0.0742	0.0680	0.91	
0.1841	0.0730	0.0704	0.94	
0.0606	0.0745	0.0737	0.98	
0.0438	0.0746	0.0740	0.99	
0.0382	0.0748	0.0743	0.99	
0.0211	0.0750	0.0747	1.00	
0.0137	0.0750	0.0748	1.00	

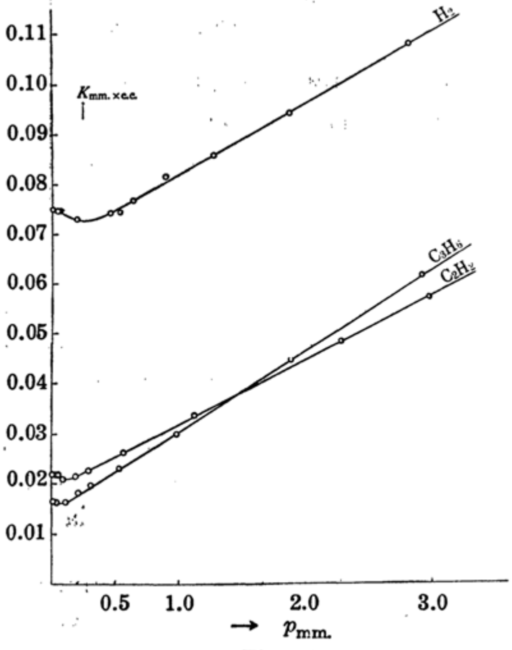


Fig. 1.

Acetylene. (20°C.)

$p_{mm.}$	K	K-ap	γ	
2.993	0.0575	0.0195	0.89	
2.284	0.0485	0.0195	0.89	
1.125	0.0336	0.0193	0.88	
0.564	0.0264	0.0192	0.87	0.88
0.287	0.0226	0.0190	0.86	
0.1824	0.0215	0.0192	0.87	
0.0913	0.0210	0.0198	0.90	
0.0453	0.0218	0.0212	0.96	
0.0239	0.0222	0.0219	1.00	
0.0119	0.0220	0.0218	0.99	
0.0066	0.0220	0.0219	1.00	

Propylene. (20°C.)

$p_{mm.}$	K	K-ap	γ	
2.940	0.0616	0.0149	0.91	
1.894	0.0448	0.0148	0.90	
0.984	0.0302	0.0147	0.90	
0.531	0.0232	0.0148	0.90	0.90
0.303	0.0197	0.0149	0.91	
0.213	0.0183	0.0149	0.91	
0.1050	0.0165	0.0148	0.90	
0.0585	0.0162	0.0153	0.93	
0.0353	0.0164	0.0158	0.96	
0.0243	0.0164	0.0160	0.98	
0.0102	0.0164	0.0162	0.99	

of Table 1. The observed values of a agree very well with the values calculated from the viscosities and this comparison is shown in Table 2.

Table 2.

	$\eta_{20^\circ}\times 10^7$	a	
		obs.	calc.
H_2	924	0.0141	0.0141
C_2H_2	1022	0.0127	0.0127
C_3H_6	848	0.0159	0.0153

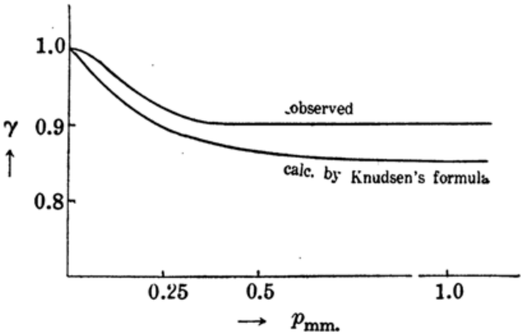


Fig. 2. γ of Hydrogen

The coefficient γ of simple gas is a function of the mean pressure and is constant at very low pressures, where it is equal to 1.0, and also constant at the pressures higher than about 0.4 mm., where it is equal to 0.9.

Hence equation (3) is the general formula over a wide range of pressures. If the pressure is so low that the mean free path of the molecule is large against the diameter of the capillary, the first term of equation (3) can be neglected and γ becomes unity, so that the formula of pure molecular flow is obtained. If the pressure is so high that the mean free path is negligible against the diameter, the second term of equation (3) is negligible and we have the formula of pure viscous flow.

Knudsen⁽³⁾ introduced empirically the following formula for γ and as the value at higher pressures gave 0.81 which is smaller than the value obtained by the present author.

$$\gamma = \frac{1+c_1 p}{1+c_2 p} \tag{5}$$

where $$c_1 = 2.00\frac{\sqrt{\rho_1}}{\eta}r, \qquad c_2 = 2.47\frac{\sqrt{\rho_1}}{\eta}r.$$

The comparison between the values of γ calculated by (5) and those observed for hydrogen is graphically shown in Fig. 2.

As seen from Fig. 2, the observed values of γ can not be appropriately expressed by Knudsen's formula.

If only a fraction f of the impinging molecules leave the wall according to the cosine law 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 $(2-f)/f$ by Smoluchowski⁽⁴⁾ and $f/(2-f)$ by Gaede.⁽⁵⁾ As described in foregoing paper, this factor is unity at the pure molecular flow. However, if we assume that f is not unity at medium pressures, it will be able to interpret, by using Gaede's factor, that γ becomes smaller than unity. This assumption of f smaller than unity at medium pressures deserves further theoretical investigation.

The existence of a minimum point of the K–p curve seems to be peculiar and has been experimentally examined by many authors. However, as seen from the results of the present author, Knudsen, and Klose,⁽⁶⁾ the existence is probably correct, notwithstanding that the theoretical interpretation has not yet been done.

There is a close connection between the decrease of the values of γ and the existence of a minimum point, and if the former can be interpreted, the latter point will be clear.

The Quantities of Flow of Gaseous Mixtures. The quantities of flow of the mixtures (K') of $H_2 \sim C_2H_2$ and $H_2 \sim C_3H_6$ were measured and the results are tabulated in Tables 3 and 4.

The shape of $K'-p$ curves of mixtures is similar to that of simple gases. As seen from the fourth columns of Tables 4 and 5, γ''s of mixtures, similarly as in the case of simple gases, become constant at higher pressures. Hence the quantity of flow of a mixture can be expressed by a formula analogous to (3), namely,

---

(3) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.
(4) M. v. Smoluchowski, *ibid.*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*. (IV). **41** (1913), 289.
(6) W. Klose, *ibid.*, (V), **11** (1931), 73.

Table 3. The Quantities of Flow of $H_2\sim C_2H_2$. (Fig. 3.)

Mixture I.

(H_2: 75.6 %, C_2H_2: 24.31%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
2.780	0.0768	0.0445	0.72	0.72
1.914	0.0665	0.0443	0.71	
1.343	0.0601	0.0445	0.72	
0.725	0.0530	0.0446	0.72	
0.4756	0.0535	0.0480	0.77	
0.2730	0.0558	0.0526	0.85	
0.1458	0.0576	0.0559	0.90	
0.0581	0.0620	0.0613	0.99	
0.0503	0.0621	0.0615	0.99	
0.0221	0.0621	0.0619	1.00	

Mixture II.

(H_2: 51.18%, C_2H_2: 48.82%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.161	0.0730	0.0356	0.73	0.73
2.064	0.0601	0.0357	0.73	
1.422	0.0525	0.0357	0.73	
0.858	0.0458	0.0357	0.73	
0.518	0.0430	0.0369	0.75	
0.3281	0.0435	0.0396	0.81	
0.2002	0.0459	0.0435	0.89	
0.1471	0.0470	0.0453	0.92	
0.0659	0.0485	0.0477	0.97	
0.0374	0.0490	0.0485	0.99	

Mixture III.

(H_2: 25.97%, C_2H_2: 74.03%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
2.886	0.0624	0.0260	0.73	0.73
1.944	0.0503	0.0258	0.73	
0.925	0.0374	0.0257	0.73	
0.694	0.0345	0.0258	0.73	
0.4154	0.0322	0.0270	0.76	
0.2260	0.0317	0.0284	0.80	
0.1374	0.0320	0.0303	0.85	
0.0276	0.0341	0.0337	0.95	
0.0187	0.0352	0.0350	0.99	
0.0113	0.0354	0.0353	0.99	

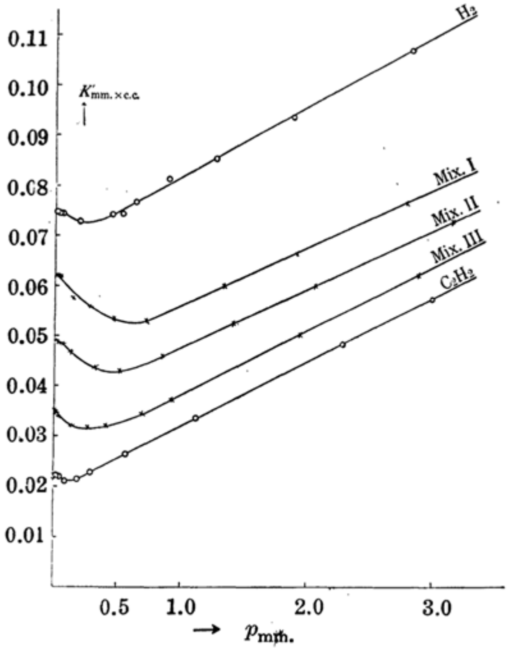


Fig. 3. $H_2\sim C_2H_2$ (20°C.)

Table 4. The Quantities of Flow of $H_2 \sim C_3H_6$. (Fig. 4.)

Mixture I.

(H_2 : 50.82%, C_3H_6 : 49.18%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.000	0.0699	0.0302	0.66	0.66
2.034	0.0570	0.0300	0.66	
0.995	0.0431	0.0299	0.65	
0.591	0.0381	0.0303	0.66	
0.3013	0.0385	0.0345	0.75	
0.2093	0.0402	0.0374	0.82	
0.0980	0.0450	0.0437	0.95	
0.0619	0.0455	0.0447	0.98	
0.0390	0.0459	0.0454	0.99	
0.0128	0.0458	0.0456	1.00	

Mixture II.

(H_2 : 75.18%, C_3H_6 : 24.82%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.008	0.0780	0.0401	0.66	0.66
1.982	0.0648	0.0398	0.65	
0.942	0.0510	0.0401	0.66	
0.710	0.0496	0.0406	0.67	
0.450	0.0518	0.0461	0.76	
0.2621	0.0550	0.0517	0.85	
0.1899	0.0588	0.0564	0.92	
0.0848	0.0603	0.0592	0.97	
0.0403	0.0609	0.0604	0.99	
0.0117	0.0610	0.0609	1.00	

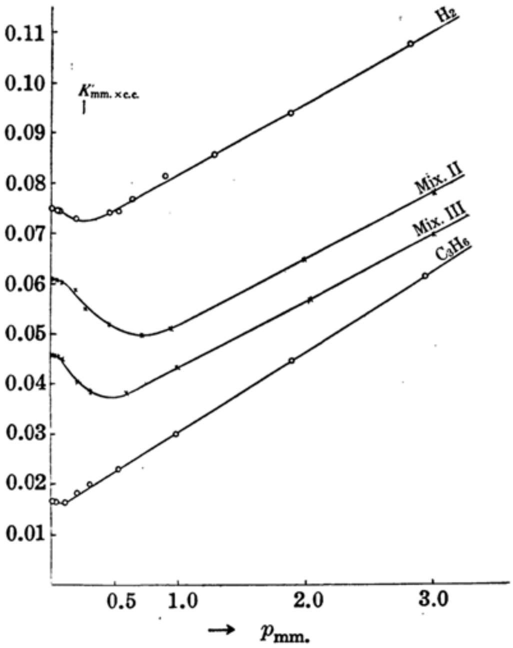


Fig. 4. $H_2 \sim C_3H_6$ (20°C.)

$$K' = a'p + \gamma' b', \tag{6}$$

where $a' = \frac{\pi}{8} \frac{1}{\eta'} \frac{r^4}{l}$, $b' = \frac{4}{3}\sqrt{2\pi}\,\frac{r^3}{l}\left(\frac{n_1}{\sqrt{\rho_1}} + \frac{n_2}{\sqrt{\rho_2}}\right)$,

n_1 and n_2 are mol fractions of components and the prime means the values of a mixture.

The comparison between the observed and calculated values of a' is given in Table 5.

Table 5.

		$\eta'_{20^\circ}\times 10^7$	a'		γ' at higher press.	
			obs.	calc.		
$H_2\sim C_2H_2$	Mixture I	1107	0.0116	0.0117	0.72	0.73
	Mixture II	1088	0.0118	0.0119	0.73	
	Mixture III	1055	0.0126	0.0123	0.73	
$H_2\sim C_3H_6$	Mixture I	1082	0.0126	0.0120	0.66	0.66
	Mixture II	1011	0.0133	0.0128	0.66	

The calculated values of a' are obtained by using the viscosities which are computed, in the case of $H_2\sim C_2H_2$, by interpolation from the observed values at 20°C. and, in the case of $H_2 \sim C_3H_6$, by the viscosity formula for the mixture, the viscosities at 20° being not observed.

The values of γ' at higher pressures of the mixtures are summarized in the last column of Table 5. These are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases.

As seen from the K'–p curves in Fig. 3 and 4, the occurrence of minimum point of mixtures is very much remarkable. It was already shown in a preceding paper that when a mixture flows through the capillary, the separation takes place at low pressures, for example at the pressures lower than about 1 mm. for the mixture $H_2\sim C_2H_2$. Owing to this separation the flow of hydrogen is comparatively larger at pressures lower than 1 mm., consequently the minimum point occurs at the pressure higher than in the case of simple gases.

The Quantities of Flow of Mixtures of Organic Vapours. The quantities of flow of the following mixtures of organic vapours were measured at the pressures lower than about 3 mm.

$$C_6H_6\sim CCl_4, \quad CCl_4\sim CHCl_3, \quad (C_2H_5)_2O\sim CHCl_3.$$

In order to increase the accuracy of measurement and to be able to compute the viscosities from K–p curves, the essential parts of the apparatus were kept in the thermostat and the McLeod gauge of short type was read by using a cathetometer. The experimental procedure is the same as described in the preceding paper.

The results of observation are shown graphically in Fig. 5–7. The flowing quantities of these mixtures can be expressed, similarly as the mixtures described above, by equation (6).

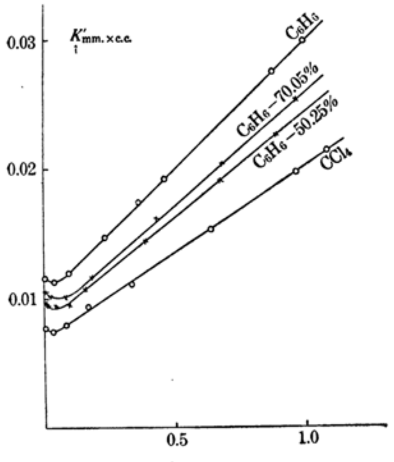


Fig. 5. $C_6H_6 \sim CCl_4$ (20°C.)

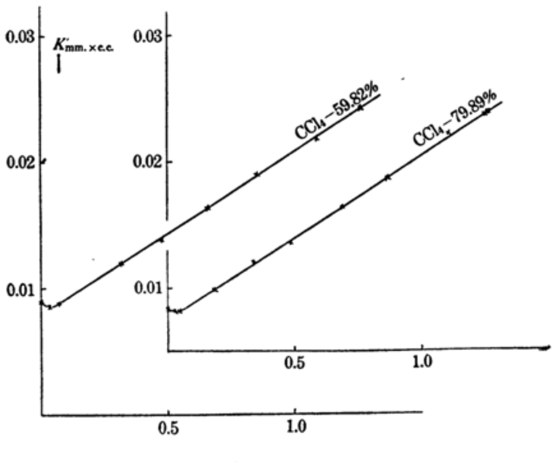


Fig. 6. $CCl_4 \sim CHCl_3$ (20°C.)

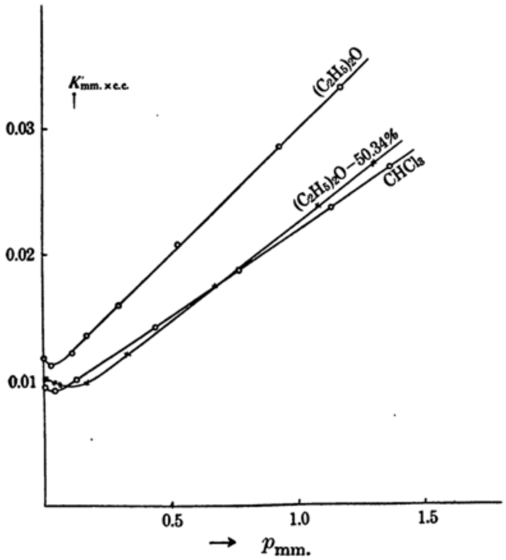
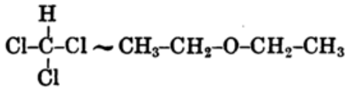
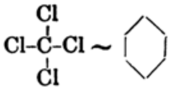
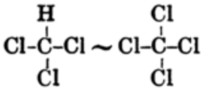


Fig. 7. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The values of γ' at higher pressures are 0.69 for $CHCl_3 \sim (C_2H_5)_2O$, 0.80 for $CCl_4 \sim C_6H_6$, and 0.89 for $CHCl_3 \sim CCl_4$. Those together with other two are summarized in Table 6. γ' are about 0.9 for simple gases but smaller for mixtures. It can be noticed that the value of γ' depends upon the configurations of two components. Namely as the configurations of $CHCl_3$ and CCl_4 are alike, the mixture of these vapours has the value of γ' nearly equal to that of a simple gas. But the values of the mixtures of $H_2 \sim C_3H_6$ and $CHCl_3 \sim (C_2H_5)_2O$, whose components are considered to have not similar configurations, are far smaller than 0.9.

Table 6. The Values of γ' at Higher Pressures.

	γ' at higher press.
$H_2 \sim CH_3\text{-}CH{=}CH_2$	0.66
 $\mathrm{Cl\text{-}\overset{H}{\underset{Cl}{C}}\text{-}Cl \sim CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3}$	0.69
$H_2 \sim CH{\equiv}CH$	0.73
 $\mathrm{Cl\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}Cl} \sim$	0.80
 $\mathrm{Cl\text{-}\overset{H}{\underset{Cl}{C}}\text{-}Cl \sim Cl\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}Cl}$	0.89
H_2	0.91
C_2H_2	0.88
C_3H_6	0.90
C_6H_6	0.87
$CHCl_3$	0.90
CCl_4	0.88
$(C_2H_5)_2O$	0.86

The Viscosities of Benzene, Carbon tetrachloride, Chloroform, Ethyl ether, and Their Mixtures. From the quantities of flow the viscosities of the vapours can be calculated by equation (4). The values at 20°C. for C_6H_6, CCl_4, $CHCl_3$, and $(C_2H_5)_2O$ are given in Table 7.

Table 7.

Vapour	$\eta \times 10^7$ at 20°C.	
	obs.	calc.
C_6H_6	662	705
CCl_4	983	939
$CHCl_3$	976	971
$(C_2H_5)_2O$	666	695

The values given in the third column of Table 7 are calculated using Sutherland's constants obtained by T. Titani.(7) The agreement of the calculated and observed values is not good. This is perhaps due to the fact that Sutherland's constants were obtained from the observations above the boiling point and this constant is not satisfactorily accurate for low temperature.

The viscosities of mixtures of $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, and $(C_2H_5)_2O \sim CHCl_3$ are given in Tables 8–10 and Fig. 6–8.

Table 8. Viscosities of $C_6H_6 \sim CCl_4$ at 20°C. (Fig. 8.)

$$\eta' = \frac{662\times10^{-7}}{1+\frac{n_2}{n_1}1.0} + \frac{983\times10^{-7}}{1+\frac{n_1}{n_2}1.0}$$

C_6H_6 %	CCl_4 %	$\eta'\times10^7$ obs.	$\eta'\times10^7$ calc.
100.00	0.00	662	662
75.05	24.95	746	740
50.25	49.75	816	822
0.00	100.00	983	983
$\alpha_1\alpha_2\beta = 1.39$, $\alpha_1\alpha_2/\beta = 0.63$			

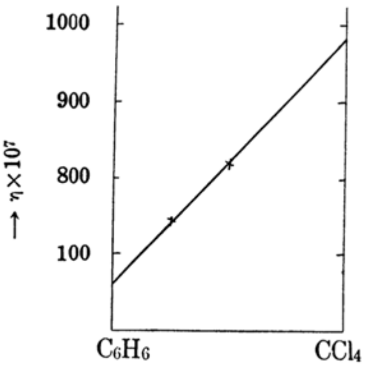


Fig. 8. $C_6H_6 \sim CCl_4$ (20°C.)

Table 9. Viscosities of $CCl_4 \sim CHCl_3$ at 20°C. (Fig. 9.)

$$\eta' = \frac{983\times10^{-7}}{1+\frac{n_2}{n_1}0.82} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.96}$$

CCl_4 %	$CHCl_3$ %	$\eta'\times10^7$ obs.	$\eta'\times10^7$ calc.
100.00	0.00	983	983
79.89	20.11	1020	1017
59.82	50.18	1038	1038
0.00	100.00	976	976
$\alpha_1\alpha_2\beta = 0.99$, $\alpha_1\alpha_2/\beta = 0.985$			

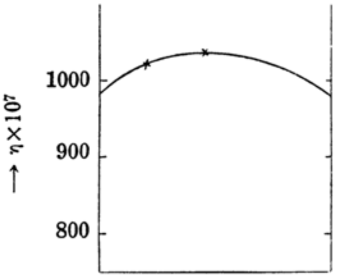


Fig. 9. $CCl_4 \sim CHCl_3$ (20°C.)

---

(7) T. Titani, this Bulletin, **8** (1933), 255.

Table 10. Viscosities of $(C_2H_5)_2O \sim CHCl_3$ at 20°C. (Fig. 10.)

$$\eta' = \frac{666\times10^{-7}}{1+\frac{n_2}{n_1}0.877} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.982}$$

$(C_2H_5)_2O$%	$CHCl_3$ %	$\eta'\times10^7$	
		obs.	calc.
100.00	0.00	666	666
50.34	49.66	848	847
0.00	100.00	976	976
$\alpha_1\alpha_2\beta = 1.425$, $\alpha_1\alpha_2/\beta = 0.66$			

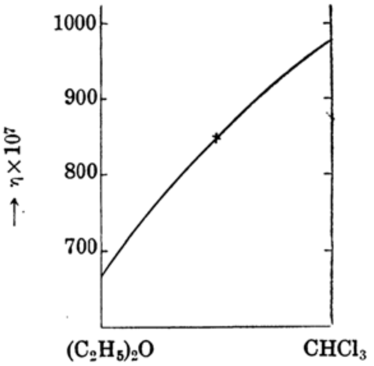


Fig. 10. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight. The occurrence of the maximum point in the case of $CCl_4 \sim CHCl_3$ is very well explained by the conditions theoretically discussed in the first paper of this series.

The values of Sutherland's constants between different molecules obtained from the viscosity data of mixtures are given in Table 11.

Table 11. Sutherland's Constants of Mixtures.

Mixture		C_1	C_2	C_{12}
1	2			
C_6H_6	CCl_4	448	365	720
CCl_4	$CHCl_3$	365	373	301
$CHCl_3$	$(C_2H_5)_2O$	373	404	352

Summary.

(1) The quantities of seven following simple gases and six gaseous mixtures flowing through the capillary have been measured at the pressures between 4 and 0.01 mm.

H_2, C_2H_2, C_3H_6, $H_2 \sim C_2H_2$, $H_2 \sim C_3H_6$;
C_6H_6, CCl_4, $CHCl_3$, $(C_2H_5)_2O$, $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$,
$(C_2H_5)_2O \sim CHCl_3$.

(2) The quantities of flow, K, is a function of the mean pressure, p, and the K–p curve passes through a minimum point. The occurrence of a minimum point of mixtures is more remarkable than in the case of simple gases.

(3) The quantities of flow of simple gases are satisfactorily expressed by

$$K = ap + \gamma b\,,$$

where γ is a coefficient which becomes a constant at higher pressures $(= 0.9)$ or at very low pressures $(= 1.0)$, and varies from 0.9 to 1.0 at the intermediate conditions.

(4) The quantities of flow of mixtures are also expressed by a formula analogous to that of simple gases. The values of γ' at higher pressures of the mixtures are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases. These values are also considered to depend on the chemical configurations of two components.

(5) The viscosities of the following mixtures have been calculated from the quantities of flow.

$$C_6H_6 \sim CCl_4\,,\qquad CCl_4 \sim CHCl_3\,,\qquad (C_2H_5)_2O \sim CHCl_3\,.$$

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight.

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

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.