THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART III.

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The determinations of the viscosity of vapours of organic compounds with the boiling points lower than ordinary room temperature were already made by the present author.(1) The similar experiment has been further continued for the determination of the viscosity of the vapours of other organic compounds such for an example as benzene, ethyl alcohol, carbon tetrachloride and etc., which are in a liquid state at room temperature.

Experimental Procedure.

The measurements of viscosity were made by the traspiration method according to the principle devised by M. Trautz and W. Weizel,(2) which will be briefly explained by using the diagrammatical figure 1. Three glass bulbs A, B and C are connected to one another with glass tubes having a large bore, and measured quantities of mercury are placed in them, as is shown in the figure. The total bulb system is heated in a thermostat to a constant temperature T_0. The lower bulb C is connected with a glass tubing to a preheating tube W and a glass capillary tube K, other end of

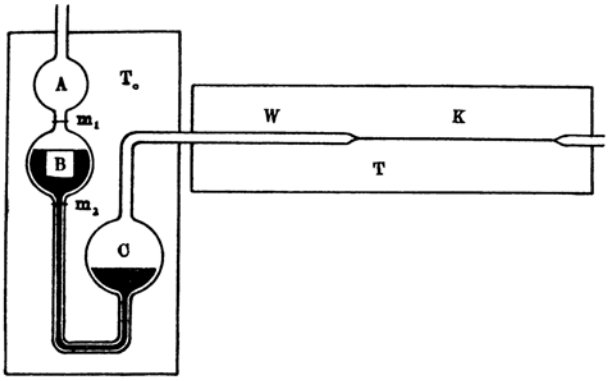

Fig. 1.

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(1) T. Titani, this Bulletin, **4** (1929), 277; **5** (1930), 98.

(2) M. Trautz & W. Weizel, *Ann. Phys.*; (4) **78** (1925), 305.

which is opened to air, both W and K being placed in another thermostat T. The vapour of organic compound is drawn through the capillary K and the preheating tube W into a space in the bulb C partially filled with mercury, by drawing up the mercury high enough into the bulbs A and B.

The vapour in the bulb C is driven out, when it attains the same temperature as that of the thermostat T_0, in the reverse direction into the air, by letting the mercury flow down from the upper bulbs A and B into the lower one C. The time t required for the mercury to travel a distance between m_1 and m_2 which are marked on the neck of the both ends of the bulb B is taken, while at the same time the temperature T of the capillary tube K, measured in the absolute scale, is recorded. Then the viscosity η of the vapour at the temperature T can be calculated by the formula⁽³⁾:

$$\eta = K\frac{t}{T} \ ,$$

where K is a constant for a given apparatus so long as the temperature T_0 of the bulb system remains constant.

The total apparatus is shown in Fig. 2. The whole system is made of glass. The two bulbs A and B are of spheroidal form and the bulb C is a sphere having the dimensions: A 25×40 mm., B 30×50 mm. and C 50×50 mm. respectively. The three bulbs are connected to one another by glass tubes 6 mm. bore, which are somewhat contracted at the points of two marks m_1 and m_2 and between the bulb B and C a small spheroidal bulb D having dimensions 15×30 mm. is inserted for the reasons which will be mentioned below. Exactly weighted quantities of mercury namely 1000 grams, are placed in the bulb system which is sealed into a large glass jacket, to be heated to a constant temperature T_0 by a toluene vapour produced in a large copper flask F. The vapour jacket supported on a strong wooden stative is covered with an asbestos plate having several windows for observation. The upper opening of the bulb A can be communicated either to a high pressure H or a suction L or it can also be opened to air M through the three stoppers X, Z or Y respectively. In a small bulb U above A are placed cotten wools in order to prevent dust particles from falling into the bulb system. The lower bulb C is jointed to a preheating tube W by sealing with a glass tube G 3 mm. bore, which is bent at three points as is shown in the figure for the purpose of buffering, and is heated electrically by winding it with a nichrom wire and by wrapping it with asbestos paper.

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(3) The derivation of this equation is referred to the original paper of M. Trautz and W. Weizel, loc. cit.

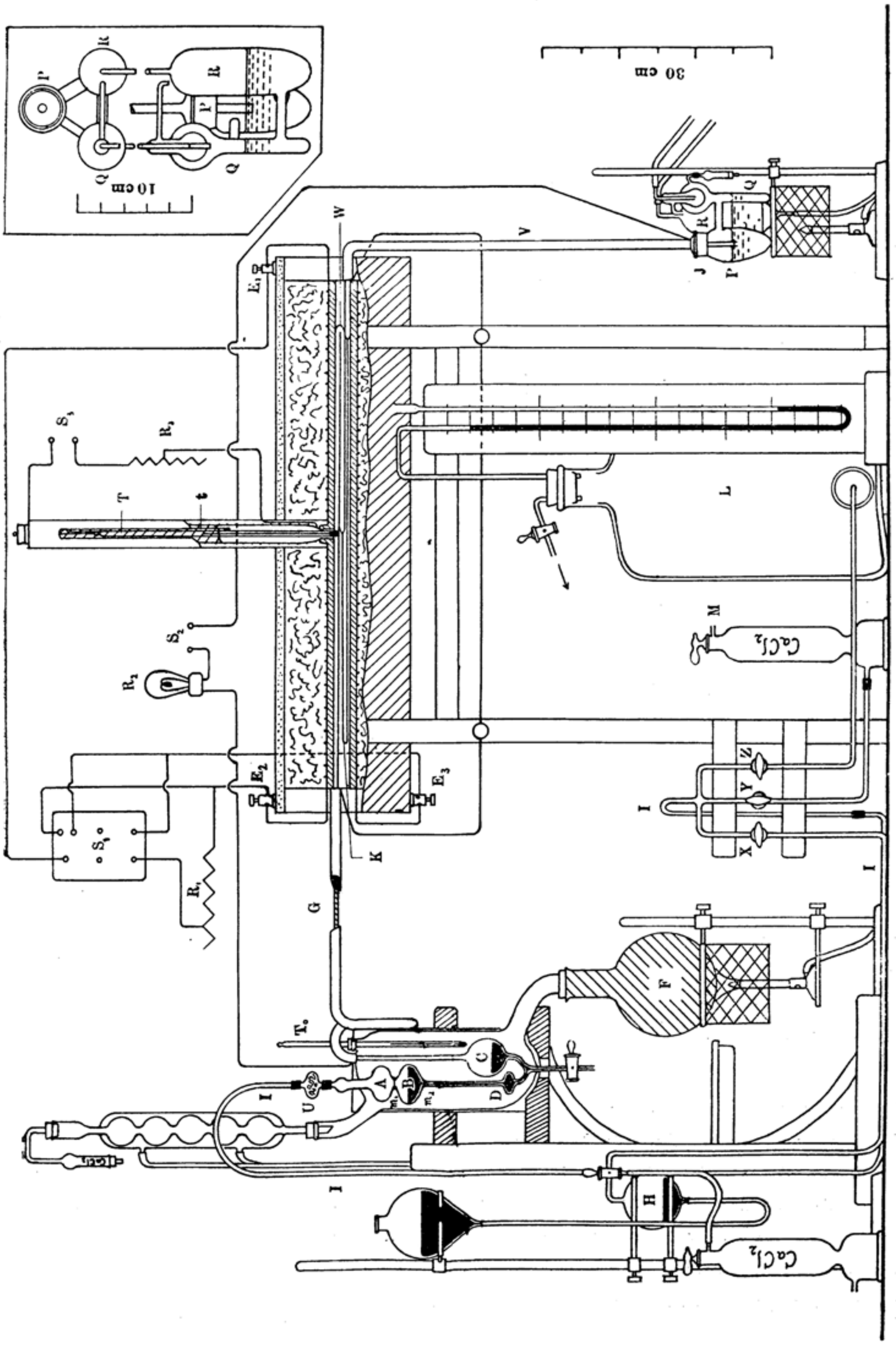
P
R
Q
10 cm
30 cm
W
V
J
E₁
E₂
E₃
S₁
S₂
S₃
R₁
R₂
R₃
T
t
K
G
T₀
A
B
C
D
U
m₁
m₂
F
H
I
L
M
X
Y
Z
CaCl₂

Fig. 2.

Both the preheating tube W 3 mm. inner diameter and 86 cm. long and the glass capillary tube K about 0.1 mm. inner diameter and 83 cm. long are bent in U-form at the points about one third the distance from the ends and sealed together at the ends of the shorter limbs. They are placed in an electrical resistance furnace, consisting of a brass pipe having a thick wall of 1 cm. and 1.5 cm. inner diameter and 68 cm. long. The outside of the pipe is wrapped with asbestos paper and then wounded with a set of nichrom wires, which are parallel to each other and which have one common terminal E_1 at one end and two separated terminals E_2 and E_3 at the other end, so that they may be communicated either in series or in parallel and also may be used quite separately by using the switch board S_1. In the latter two cases the current can be regulated by the resistance R_1. The brass pipe is once more thickly covered with asbestos and is placed centrally in a large asbestos cylinder, the space between them being packed with asbestos wools. On the middle parts of both the outer asbestos cylinder and the inner brass tube are drilled holes to be used for inserting a thermometer T to measure the temperature of the furnace. The following device is made in order to minimize for the mercury column of the thermometer T not in direct contact with the chamber of the resistance furnace the temperature corrections which would be remarkably large at high temperatures. On the middle part of the column of the thermometer T is held another small thermometer t. These two thermometers are placed within a glass cylinder wrapped with asbestos paper over which a nichrom wire is wounded for heating purpose. Another glass cylinder of larger size wrapped with asbestos is placed over them. This whole system is heated electrically by means of nichrom wire wounded over the inner glass cylinder, the switch S_3 and the resistance R_3, to a known temperature which is easily read by the second thermometer t held on to the middle part of the first larger one T as is mentioned just before. In these two respective asbestos covering the two glass cylinders are made windows through which reading on the thermometers is made possible.

The end of the capillary tube K is sealed to a long glass tube V 3 mm. inner diameter, which is bent vertically downward to be connected to a vapourising device PQR with a ground joint J. The vertical tube V wrapped with asbestos has a doubly winding of nichrom wires so as to make electrical heating connection in series with that of the glass tube G by means of the switch S_2 and the resistance R_2. The vapourising apparatus consists of this vertical tube V together with a bulb apparatus PQR, which is separately shown in the upper corner of the right hand side of Fig. 2. The organic liquid the vapour of which is to be investigated is placed in the bulbs PQR, which are gently warmed either with a small Bunsen burner or with an incandescent lamp. The loss of the liquid placed in the bulbs PQR through evaporation must be prevented and the entry of dust particles into it has to be also made impossible. For this purpose, over the bulb Q is fitted a water condenser whose running water is also used to cool the bulb R.

The lower end of the vertical tube V is placed few millimeter below the surface of the organic liquid in the bulb P, so that the liquid may run up into the vertical tube V, when we connect the upper opening of the bulb A to the suction L by carefully opening the stopper Z. But, as the tube V is electrically heated, the liquid is vapourised as soon as it run up into the tube V, the organic vapour thus produced being drawn through both the capillary and the preheating tube and finally collected over the mercury in the bulb C. When sufficient quantities of vapour are collected in the bulb C, this mixture of air and the organic vapour is pushed back through the capillary tube into the bulb P, by the pressure brought about by letting the mercury flow down first from the bulbs A and B to C and then by the further pressure obtained by the opening of the stopper X to the high pressure bulb H, which process results in bringing down the level of the mercury finally into the small bulb D. The organic vapour is then again drawn into the bulb C and when sufficient quantities of vapour get into it, they are pushed back by applying the pressure to the bulb C, as is mentioned above. With the repetition of this process number of times, the air in the whole system is gradually driven out by the organic vapour. As the total volume of the tube system is only one tenth as compared with the volume of the bulb C, the replacement of air with the organic vapour by means of this method is very easy. As a matter of fact, the time required for the mercury to pass a distance between the two marks m_1 and m_2 becomes practically constant only after repetition of such processes five times. The present author has repeated the process at least ten times before the beginning of the actual measurement. Therefore it may be quite justified in stating that the system is filled with pure vapour of the organic compound.

When sufficient quantities of vapour are collected over the mercury in the bulb C, after waiting for a while, about 15 minutes being found to be sufficient in addition to the time required for the collection of the vapour in the bulb C for the vapour to attain the temperature of the bath T_0, the vapour is finally driven back through the preheating tube W, the capillary K and vertical tube V into the liquid placed in the bulb apparatus PQR, with the pressure brought about by the mercury flowing from the bulbs A and B down to C. The time required for the mercury to pass the distance between two marks m_1 and m_2 is measured by a stop watch and this observed value is reduced to an ideal value by adding some corrections which will be discussed below. The temperature T of the electrically heated thermostat, in which the capillary is placed, is regulated and is read every three minutes during the run and the average of these readings is adopted after being corrected for the exposed column, which is greatly diminished with the devices mentioned before.

The whole apparatus is carefully cleaned before each experiment with nitric acid and chromic mixture. It is then thoroughly washed with distilled water, alcohol and benzene and finally dried by passing dry air through the whole system alternatively in opposite directions. It will also be noted here, that when the experiment is interrupted the liquid in the bulb apparatus PQR must be drawn up into the one bulb R until the lower end of the vertical tube V becomes clear off the surface of the liquid. Otherwise, the liquid gets easily up into the measuring apparatus in the liquid form, thereby giving rise to a trouble, when the total system is cooled down.

Results of Experiments.

The viscosity η of the vapour at the absolute temperature T can be computed by means of the following formula:

$$\eta = K\frac{t}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

where t is the time required for the mercury to travel a distance between the marks m_1 and m_2, T the temperature of the capillary measured in the absolute scale and K a constant for a given apparatus. But as this formula is derived by supposing ideal conditions, some corrections have to be applied in the actual case either to the time t or the constant K. The present author has applied them to the observed value of t. The corrections to be made are as follows:

(1) The correction due to the fluctuation of the temperature T_0 of the bulb C from the mean value $(108.0+273.1°$ abs.$)$:

$$\Delta_1 = \pm \Delta T_0 / T_0 = \pm 0.26\% \,/\, \pm 1°\mathrm{C}.$$

(2) The correction due to the fluctuation of the barometer readings from the mean value 760 mm. was experimentally determined and found to be:

$$\Delta_2 = \pm 0.012\% \,/\, \pm 1\,\mathrm{mm}.$$

(3) The correction due to the thermal expansion of the glass capillary tube when its temperature T is different from the standard temperature $(115.0+273.1°\text{ abs.})$:

$$\varDelta_3 = 3\alpha(T-388.1) = \pm 0.0025\% \,/\, \pm 1°\text{C.},$$

where α is a linear expansion coefficient of glass.

(4) The correction due to the kinetic energy of the vapour in the capillary tube has been calculated from the consideration that the amount of the energy lost due to the molecular friction of the vapour in the capillary being equal to the total energy of the vapour entering the capillary minus the amount of the kinetic energy possesed by the vapour at the outlet of the capillary tube, and it has been found to be:

$$\varDelta_4 = \frac{1}{K}\,\frac{V}{8\pi l.R.T}\cdot\frac{T.M}{t^2} = 0.00557\frac{T.M}{t^2} \quad \ldots\ldots\ldots\ (2)$$

where V is the total volume of the vapour transpired during the time t, l the length of the capillary, R the gas constant, M the molecular weight and T the temperature of the vapour.

(5) The correction due to the deviation from the ideal gas state of the organic vapour employed(5):

$$\varDelta_5 = \frac{1}{RT_0}\Big(\frac{a}{RT_0}-b\Big)\frac{\alpha}{760} - \frac{2}{3RT}\Big(\frac{a}{RT}-b\Big)\frac{\beta}{760} \quad \ldots\ldots\ (3),$$

where a and b are constants in the van der Waals equation, T the temperature of the capillary, T_0 that of the bulb C, α and β being constants for a given apparatus. For the present apparatus they have been found to be: $\alpha = 880$, $\beta = 1210$.

These corrections were made to the directly observed values of the time of passage t, and the reduced values of t thus obtained were put in the formula (1) to compute the viscosity η. The constant K in eq. (1) was determined experimentally by using air as a standard substance which has given 1023 sec. at 115.0°C. to the value for reduced t. At this temperature the viscosity of air(6) is known to be $\eta = 2234\times10^{-7}$. Therefore

$$K = \frac{\eta\times T}{t} = \frac{2234\times10^{-7}\times(115.0+273.1)}{1023} = 0.8453\times10^{-4}.$$

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(5) The derivation of this equation is referred to the original paper of M. Trautz and W. Weizel, loc. cit.

(6) T. Titani, loc. cit.

At the same time the apparatus has been tested by making measurements at several temperatures between 115.0° and 278.9°C. using air as a specimen. And from these data together with those obtained in the preceding paper (loc cit.) for Sutherland's constant 107 and for Reinganum's constant 84 were obtained. Then the measurements were continued for the other organic compounds.

The specimen used were all obtained from reliable commercial sources and carefully purified in the ordinary way. Their purity were checked by measuring the normal boiling points: *n*-pentane, 33.5°±3.2; *n*-hexane, 69.0°±0.3; hexamethylene, 80.9°±0.3; benzene, 80.1°±0.0; methyl acetate, 57.0°±0.2; ethyl acetate, 77.1°±0.1; ethyl ether, 34.55°±0.05; methyl alcohol, 64.65°±0.05; ethyl alcohol, 78.3°±0.0; *n*-propyl alcohol, 97.1°±0.1; isopropyl alcohol, 82.25°±0.05; acetone, 56.05°±0.05; chloroform, 61.05° ±0.05; carbon tetrachloride, 76.7°±0.0; carbon disulphide, 46.2°±0.0.

The results of the measurements for benzene and carbon tetrachloride vapour are shown in Tables 1 and 2 as examples.

Table 1.

Benzene.

$T-273.1$	t observed	Corrections %			t reduced	$\eta.10^7$
		$\Delta_1+\Delta_2+\Delta_3$	Δ_4	Δ_5		
131.2°	494.3	+0.07	−0.07	+0.36	496.1	1031
161.3	569.6	+0.19	−0.05	+0.57	573.6	1110
194.6	660.6	+0.23	−0.04	+0.75	666.8	1198
221.9	737.8	+0.19	−0.04	+0.89	745.5	1266
252.5	828.6	+0.39	−0.03	+1.00	839.9	1343
279.9	909.6	+0.46	−0.03	+1.09	923.4	1404
312.8	1017.4	+0.54	−0.02	+1.18	1034.7	1484

Table 2.

Carbon tetrachloride.

$T-273.1$	t observed	Corrections %			t reduced	$\eta.10^7$
		$\Delta_1+\Delta_2+\Delta_3$	Δ_4	Δ_5		
127.9°	630.2	−0.02	−0.09	+0.35	631.7	1334
169.3	759.7	+0.08	−0.07	+0.65	764.7	1463
200.2	865.1	+0.17	−0.06	+0.83	873.2	1562
237.2	993.9	+0.30	−0.05	+0.99	1006.2	1669
282.2	1168.1	+0.39	−0.04	+1.17	1185.9	1808
314.9	1299.0	+0.50	−0.03	+1.24	1321.2	1902

The results of the experiments are tabulated below, together with the calculated value of viscosity either with the Sutherland's or with Reinganum's formula:

$$\eta = K\frac{\sqrt{T}}{1+\frac{C}{T}} \quad \text{(Sutherland)} \quad \dots\dots\dots\dots \quad (4),$$

$$\eta = K'\frac{\sqrt{T}}{e^{\frac{C'}{T}}} \quad \text{(Reinganum)} \quad \dots\dots\dots\dots \quad (5).$$

The constants K, C in eq. (4) and K', C' in eq. (5) were computed by means of the method of least square from the observed data of viscosity. The agreement with the observed values is found to be equally good in both cases.

Table 3.

Air. (Free from carbon dioxide and moisture).

$K = 144.4\times10^{-7}$, $C = 106.8$; $K' = 140.8\times10^{-7}$, $C' = 84.3$

Temperature Centigrade	$\eta\times10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
20.0°(7)	1809	1812	1809
40.0	1897	1906	1904
60.0	2007	1999	1996
80.0	2079	2084	2085
100.0	2169	2169	2171
115.0	2234	2231	2233
133.0	2302	2305	2306
135.1	2315	2313	2315
175.2	2480	2470	2471
227.1	2665	2662	2662
278.9	2835	2843	2841

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(7) The data between 20.0° and 100.0°C. were taken from the preceding paper. (T. Titani, loc. cit.).

Table 4.

Normal pentane.

$$K = 90.30 \times 10^{-7},\ C = 382.8;\ K' = 78.32 \times 10^{-7},\ C' = 212.4$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.6°	911	911	909
158.9	995	995	996
189.6	1064	1063	1065
219.1	1126	1127	1129
249.5	1191	1192	1193
277.1	1250	1249	1249
305.9	1307	1308	1306

Table 5.

Normal hexane.

$$K = 92.16 \times 10^{-7},\ C = 436.1;\ K' = 77.83 \times 10^{-7},\ C' = 228.3$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
120.7°	866	868	865
160.8	958	957	958
188.9	1021	1019	1021
220.1	1088	1086	1088
248.0	1144	1145	1147
280.4	1213	1213	1212
306.6	1265	1266	1264

Table 6.

Hexamethylene (Cyclohexane).

$$K = 86.95 \times 10^{-7},\ C = 350.9;\ K' = 76.56 \times 10^{-7},\ C' = 201.6$$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.7°	913	915	913
154.0	987	987	987
188.3	1064	1061	1063
218.1	1124	1124	1126
248.9	1189	1188	1189
278.5	1245	1248	1248
306.4	1305	1304	1302

Table 7.

Benzene.

$K = 108.2 \times 10^{-7}$, $C = 447.5$; $K' = 90.81 \times 10^{-7}$, $C' = 231.2$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
131.2°	1031	1033	1031
161.3	1110	1111	1112
194.6	1198	1196	1198
221.9	1266	1265	1267
252.5	1343	1340	1341
279.9	1404	1407	1406
312.8	1484	1485	1482

Table 8.

Methyl acetate.

$K = 122.9 \times 10^{-7}$, $C = 501.8$; $K' = 100.4 \times 10^{-7}$, $C' = 245.9$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
143.3°	1139	1137	1136
177.7	1236	1235	1236
218.5	1348	1348	1351
248.2	1429	1429	1431
277.9	1508	1509	1509
306.6	1583	1586	1582

Table 9.

Ethyl acetate.

$K = 114.7 \times 10^{-7}$, $C = 504.0$; $K' = 93.58 \times 10^{-7}$, $C' = 246.1$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
128.1°	1018	1018	1015
158.6	1098	1099	1100
192.9	1195	1189	1192
218.3	1250	1255	1257
248.6	1332	1332	1334
280.1	1409	1411	1411
313.7	1497	1495	1491

Table 10.

Ethyl ether.

$K = 100.3 \times 10^{-7}$, $C = 404.0$; $K' = 86.36 \times 10^{-7}$, $C' = 220.5$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.8°	983	985	982
159.4	1079	1079	1079
189.9	1152	1153	1154
217.7	1222	1219	1221
251.0	1300	1297	1298
277.8	1358	1358	1359
308.9	1425	1428	1427

Table 11.

Methyl alcohol.

$K = 145.7 \times 10^{-7}$, $C = 486.9$; $K' = 119.0 \times 10^{-7}$, $C' = 237.8$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
111.3°	1259	1260	1257
153.9	1408	1407	1409
188.8	1527	1525	1529
217.5	1620	1620	1624
250.0	1725	1726	1728
277.6	1815	1815	1813
311.5	1921	1922	1916

Table 12.

Ethyl alcohol.

$K = 117.6 \times 10^{-7}$, $C = 407.3$; $K' = 101.2 \times 10^{-7}$, $C' = 222.3$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
130.2°	1173	1175	1170
170.7	1293	1292	1293
191.8	1355	1352	1353
217.5	1421	1423	1426
251.7	1519	1517	1520
278.2	1585	1588	1588
308.7	1670	1669	1667

Table 13.

Normal propyl alcohol.

$K=119.1\times10^{-7}$, $C=515.6$; $K'=95.50\times10^{-7}$, $C'=243.5$

Temperature Centigrade	$\eta\times10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.7°	1025	1026	1024
149.0	1102	1102	1102
179.8	1186	1185	1187
209.7	1267	1266	1267
243.2	1350	1354	1354
273.0	1434	1432	1429

Table 14.

Iso-propyl alcohol.

$K=113.2\times10^{-7}$, $C=459.9$; $K'=94.13\times10^{-7}$, $C'=233.0$

Temperature Centigrade	$\eta\times10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
119.2°	1028	1032	1030
121.3	1034	1038	1036
138.4	1084	1085	1084
149.2	1112	1114	1114
169.4	1169	1168	1170
190.7	1231	1224	1227
192.9	1237	1230	1233
198.4	1248	1245	1247
218.3	1299	1297	1299
235.1	1340	1340	1342
251.1	1382	1381	1382
279.2	1450	1452	1451
293.1	1488	1487	1484
307.9	1517	1523	1519

Table 15.

Acetone.

$K = 119.2 \times 10^{-7}$, $C = 541.5$; $K' = 95.45 \times 10^{-7}$, $C' = 254.7$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
119.0°	991	992	987
159.5	1101	1101	1102
190.4	1186	1184	1186
217.3	1253	1255	1258
247.7	1334	1334	1336
278.8	1416	1414	1414
306.4	1481	1484	1481

Table 16.

Chloroform.

$K = 132.9 \times 10^{-7}$, $C = 373.0$; $K' = 115.4 \times 10^{-7}$, $C' = 207.6$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
121.3°	1357	1356	1354
161.3	1491	1490	1492
189.1	1579	1581	1584
218.7	1674	1676	1678
250.0	1776	1774	1775
279.4	1868	1865	1863
307.5	1947	1950	1945

Table 17.

Carbon tetrachloride.

$K = 127.1 \times 10^{-7}$, $C = 365.4$; $K' = 110.9 \times 10^{-7}$, $C' = 205.6$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
127.9°	1334	1332	1331
169.3	1463	1464	1466
200.2	1562	1561	1563
237.2	1669	1673	1675
282.2	1808	1807	1805
314.9	1902	1901	1896

Table 18.

Carbon disulphide.

$K = 151.1 \times 10^{-7}$, $C = 499.5$; $K' = 122.7 \times 10^{-7}$, $C' = 241.3$

Temperature Centigrade	$\eta \times 10^7$		
	Observed	Calculated (Sutherland)	Calculated (Reinganum)
114.3°	1303	1299	1296
152.8	1434	1436	1438
190.2	1561	1565	1570
228.2	1692	1695	1698
267.3	1830	1826	1826
309.8	1966	1965	1959

Some results of the present author are compared with those of the other observers. The values of viscosity observed by the author at 100°C. are listed together with those of the other observers in Table 19.

Table 19.

Viscosity at 100°C. $\times 10^{-7}$.

Substance	Author's	Other observers'
Normal pentane	859	841 (Bleakney 1932)(8)
Normal hexane	818	——
Hexamethylene	864	880 (Nasini 1929)(9)
Benzene	947	1176 (Schumann 1884)(10) 930 (Rappenecker 1910)(11) 940 (Nasini 1929)
Methyl acetate	1008	1015 (Rappenecker 1910)
Ethyl acetate	939	955 (,,)
Ethyl ether	927	942 (Pedersen 1907)(12) 967 (Rappenecker 1910)
Methyl alcohol	1218	——
Ethyl alcohol	1082	1088 (Pedersen 1907) 1090 (Rappenecker 1910)
Normal propyl alcohol	964	——
Iso-propyl alcohol	977	——
Acetone	936	943 (Rappenecker 1910)

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(8) Bleakney, *Physics*, **3** (1932), 123.

(9) Nasini, *Proc. Roy. Soc. London*, A**123** (1929), 692.

(10) Schumann, *Wied. Ann.*, **23** (1884), 353.

(11) Rappenecker, *Z. physik. Chem.*, **72** (1910), 695.

(12) Pedersen, *Phys. Rev.*, **25** (1907), 225.

Table 19.—(*Concluded*)

Substance	Author's	Other observers'
Chloroform	1281	1307 (Rappenecker 1910) 1244 (Braune & Linke 1930)(13)
Carbon tetrachloride	1238	1164 (,,) 1203 (Sperry & Mack 1932)(14)
Carbon disulphide	1245	1218 (Bleakney 1932)

The agreement between the values of the author and those of the other observers is generally good except few cases.

The Sutherland's and Reinganum's constants obtained by the author are listed in Tables 20 and 21 respectively, together with those reported by the other observers. Large differences between the values of the author and those of the other observers are often found. But it must be taken

Table 20.

Sutherland's constants.

Substance	Author's	Other observers'(15)
Normal pentane	383	299 (Bleakney 1932)
Normal hexane	436	——
Hexamethylene	351	330 (Nasini 1929)
Benzene	448	700 (Rappenecker 1910) 380 (Nasini 1929)
Methyl acetate	502	660 (Rappenecker 1910)
Ethyl acetate	504	650 (,,)
Ethyl ether	404	325 (,,)
Methyl alcohol	487	——
Ethyl alcohol	407	525 (Rappenecker 1910)
Normal propyl alcohol	516	——
Iso-propyl alcohol	460	——
Acetone	542	670 (Rappenecker 1910)
Chloroform	373	292 (,,) 462 (Braune & Linke 1930)
Carbon tetrachloride	365	492 (,,) 335 (Sperry & Mack 1932)
Carbon disulphide	500	——

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(13) Braune and Linke, *Z. physik. Chem.*, **A148** (1930), 195.

(14) Sperry and Mack, *J. Am. Chem. Soc.*, **54** (1932), 904.

(15) loc. cit.

Table 21.

Reinganum's constants.

Substance	Author's	Other observers'(16)
Normal pentane	212	———
Normal hexane	228	———
Hexamethylene	202	———
Benzene	231	260 (Rappenecker 1910)
Methyl acetate	246	258 (,,)
Ethyl acetate	246	260 (,,)
Ethyl ether	221	180 (,,)
Methyl alcohol	238	———
Ethyl alcohol	222	210 (Rappenecker 1910)
Normal propyl alcohol	244	———
Iso-propyl alcohol	233	———
Acetone	255	251 (Rappenecker 1910)
Chloroform	208	173 (,,)
Carbon tetrachloride	206	———
Carbon disulphide	241	———

into consideration that in determining the values for Sutherland's and Reinganum's constants, the method based on the data at few successive temperatures, as was done by Rappenecker, would be more liable to lead to great errors than the method in which a greater number of observations are made.

J. Arnold(17) has recently pointed out that the Sutherland's constants can be calculated from the viscosity determination at a single temperature T by the use of the molecular diameter calculated from the molecular volume V_S at boiling point, according to the formula:

$$C^* = 2.70 \times 10^{-5} (M^{\frac{1}{2}}\ T^{\frac{3}{2}} / \eta V_S^{\frac{2}{3}}) - T \quad \ldots\ldots\ldots\ldots\ldots \quad (6),$$

where M means molecular weight. The values of C^* calculated from the viscosity data at 100°C. are listed in Table 22 together with the values of C computed by the ordinary method. The agreement between C and C^* is generally good, average deviation being 5%, except few cases i.e. hexamethylene, methyl alcohol, chloroform and carbon tetrachloride.

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(16) Rappenecker, loc. cit.

(17) J. H. Arnold, *J. Chem. Phys.*, **1** (1933) 170.

Table 22 contains also the values of Sutherland's constants calculated according to the rules of Rankine(18) and Vogel(19), the Sutherland's constant being found to be roughly proportional either to the critical temperature T_K or to the boiling point T_S, both of which are measured in the absolute scale;

$$C = T_K / 1.12 \quad \text{(Rankine)} \quad \dots\dots\dots\dots\dots\dots \quad (7),$$

$$C = 1.47\, T_S \quad \text{(Vogel)} \quad \dots\dots\dots\dots\dots\dots \quad (8).$$

Table 22.

Sutherland's constants.

Substance	C	C^*	$T_K / 1.12$	$1.47\, T_S$
Normal pentane	383	427	420	454
Normal hexane	436	446	454	503
Hexamethylene	351	494	494	521
Benzene	448	492	501	519
Methyl acetate	502	494	453	485
Ethyl acetate	504	495	467	515
Ethyl ether	404	432	417	453
Methyl alcohol	487	366	458	497
Ethyl alcohol	407	405	461	516
Normal propyl alcohol	516	459	479	549
Iso-propyl alcohol	460	452	461	522
Acetone	542	501	454	484
Chloroform	373	489	479	491
Carbon tetrachloride	365	510	496	515
Carbon disulphide	500	496	494	469

The agreement with the observed values seems to be better for the Rankine's formula than for that of Vogel.

Collision Diameter.

The collision diameters of the molecules were computed by using the following equations all of which are derived from the kinetic theory of gases(20):

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(18) Rankine, *Proc. Roy. Soc. London,* A **84** (1910), 181.

(19) Vogel, *Ann. Phys.,* **43** (1914), 1235.

(20) Kuenen, „Die Eigenschaften der Gase", (1919), p. 136.

$$\bar{u}^2 = \frac{8}{\pi}\frac{p}{d} = \frac{8}{\pi} \times 1013250 \times \frac{30619}{M} \quad \ldots\ldots\ldots\ldots\ldots \text{(9)},$$

$$l = \frac{32\eta}{5\pi d\bar{u}} = \frac{\eta \times 30619}{0.49 \times M \times \bar{u}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(10)},$$

$$\sigma^2 = \frac{1}{\sqrt{2}\, n\pi l F(T)}, \quad (n = 2.0 \times 10^{19}) \quad \ldots\ldots\ldots \text{(11)},$$

where

$$F(T) = 1 + \frac{C}{T} \quad \text{(Sutherland)} \quad \ldots\ldots\ldots\ldots\ldots \text{(12)},$$

or

$$F(T) = e^{\frac{C'}{T}} \quad \text{(Reinganum)} \quad \ldots\ldots\ldots\ldots\ldots \text{(13)},$$

and the symbols in the equations have the following meanings:

$\bar{u}$: mean velocity of the molecule at 100°C.,
p: atmospheric pressure,
d: density of the vapour at 100°C. and under the atmospheric pressure,
M: molecular weight,
l: mean free path of the molecule at 100°C. and under the atmospheric pressure,
η: viscosity of the vapour at 100°C.,
σ: collision diameter of the molecule,
n: number of molecules contained in 1 c.c. at 100°C. and under the atmospheric pressure.

The results of the calculation are listed in Tables 23 and 24, where σ_S means the molecular diameter calculated by the use of the Sutherland's formula (12) and σ_R that of Reinganum (13). The molecular diameter can also be computed from the constant b in the van der Waals equation⁽²¹⁾ namely:

$$\sigma_b = \frac{3}{2}\frac{b}{N_A \pi}, \quad (N_A = 6.06 \times 10^{23}) \quad \ldots\ldots\ldots\ldots \text{(14)},$$

where N_A means the Avogadro's constant. The values σ_b are given in the forth column of Table 24, and it will be seen in most cases that σ_b is nearly equal to σ_S. The last column of Table 24 contains the cube root of the molecular volume V_S at boiling point, which may be proportional to σ_S, as it was already pointed out in the preceding paper⁽²²⁾. It

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(21), (22) T. Titani, loc. cit.

Table 23.

Substance	M	$\bar{u}$	$\eta \cdot 10^7$	$l \cdot 10^8$	C	C'
Normal pentane	72.10	33100	859	225	383	212
Normal hexane	86.11	30290	818	196	436	228
Hexamethylene	84.10	30650	864	210	351	202
Benzene	78.05	31820	947	238	448	231
Methyl acetate	74.05	32660	1008	260	502	246
Ethyl acetate	88.06	29950	939	223	504	246
Ethyl ether	74.08	32660	927	239	404	221
Methyl alcohol	32.03	49660	1218	478	487	238
Ethyl alcohol	46.05	41420	1082	355	407	222
Normal propyl alcohol	60.06	36270	964	277	516	244
Iso-propyl alcohol	60.06	36270	977	280	460	233
Acetone	58.05	36890	936	273	542	255
Chloroform	119.39	25720	1281	261	373	208
Carbon tetrachloride	153.84	22660	1238	222	365	206
Carbon disulphide	76.12	32220	1245	317	500	241

Table 24.

Substance	$\sigma_S \times 10^8$ (Sutherland)	$\sigma_R \times 10^8$ (Reinganum)	$\sigma_b \times 10^8$ (From b)	Cube root of Mol. Vol. at B.P. $\sqrt[3]{V_S}$
Normal pentane	5.00	5.35	4.86	4.90
Normal hexane	5.18	5.61	5.18	5.19
Hexamethylene	5.19	5.63	4.83	4.88
Benzene	4.66	5.07	4.56	4.58
Methyl acetate	4.32	4.76	4.46	4.38
Ethyl acetate	4.67	5.15	4.81	4.73
Ethyl ether	4.78	5.13	4.73	4.74
Methyl alcohol	3.21	3.55	3.75	3.50
Ethyl alcohol	3.92	4.21	4.05	3.96
Normal propyl alcohol	4.16	4.63	4.42	4.34
Iso-propyl alcohol	4.27	4.66	4.26	4.33
Acetone	4.12	4.59	4.19	4.26
Chloroform	4.67	5.01	4.32	4.39
Carbon tetrachloride	5.09	5.44	4.64	4.70
Carbon disulphide	3.92	4.34	3.93	3.96

is actually the case for most compounds listed in Table 24 except few cases. The compounds whose molecules are of extremely non-polar nature, such as hexamethylene, chloroform and carbon tetrachloride seem to give σ_S too large a value as compared with σ_b or $\sqrt[3]{V_S}\cdot 10^{-8}$. However, for the compounds of strong polar nature such as methyl alcohol the reverse is the case. These differences must result either from the function *F(T)* in eq. (11) or more directly from the Sutherland's constant *C* in *F(T)*, which measures the work required to separate two molecules from each other against the intermolecular attraction.

The collision diameter of benzene seems to be interesting in relation to its magnitude. It has become clear not only from the X-ray crystallographical study but also from the thermochemical investigations that the benzene nucleus is the same as the hexagonal carbon atom lattice in graphite, the length of the one side of this hexagonal model being found to be 2.45 Å. Therefore, its diameter is equal to $2 \times 2.45 = 4.9$ Å, when we assume the model to have a regular form. This value is very nearly equal to the collision diameter of benzene, $\sigma = 4.7 - 5.1$ Å deduced from the viscosity measurement in the present research.

The experimental part of the present research was carried out between April 1929 and April 1930 in the Katayama Laboratory of the Institute of Physical and Chemical Research, Hongo, Tokio. The delay of the publication is mainly due to the trip which the author made in Europe.

The author wishes to express his cordial thanks to Prof. Katayama for his interest and encouragement taken in this research.

Summary.

(1) An apparatus, based on the principle of Trautz and Weizel, was constructed for measuring the viscosity of vapours.

(2) With this apparatus the viscosity of vapours of the following substances were measured at temperatures between about 120° and 300°C.: air, *n*-pentane, *n*-hexane, hexamethylene, benzene, methyl acetate, ethyl acetate, ethyl ether, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, iso-propyl alcohol, acetone, chloroform, carbon tetrachloride and carbon disulphide.

(3) From these measurements the constants of both Sutherland and Reinganum as well as collision diameters of molecules were calculated.

(4) The collision diameters calculated from viscosity data were found to be nearly equal to those computed from the constants *b* in the

van der Waals equation and they came out to be proportional to the cube roots of molecular volumes at boiling points, as was already pointed out in the preceding paper except few cases.

(5) Values obtained for collision diameters of non-polar compounds such as carbon tetrachloride and hexamethylene seem to be too large and those for strong polar compounds such as methyl alcohol too small as compared with the values of molecular diameters computed from *b* or from the molecular volumes at boiling points.

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