THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART V.

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In the preceding papers(1) it has been shown that the relation between the molecular fluidity Φ defined as the reciprocal of the product of viscosity η and molecular distance $V^{\frac{1}{3}}$, and molecular volume V or temperature T can be expressed by the following simple equations;

$$\Phi=K(V^{\frac{2}{3}}-B^{\frac{2}{3}}) \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\Phi_K-\Phi=C\,(T_K-T)^{\frac{1}{5}} \quad \ldots\ldots\ldots\ldots \quad (2)$$

where K, B and C are arbitrary constants, and Φ_K the value of Φ at the critical temperature T_K.

Eliminating Φ from equations (1) and (2) the relation:

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(1) Part I, this Bulletin, **2** (1927), 95; II, ibid, 161; III, ibid, 196; IV, ibid, 225.

$$V_K^{\frac{2}{3}}-V^{\frac{2}{3}}=A\ (T_K-T)^{\frac{1}{5}}\ \ldots\ldots\ldots\ldots\ (3)$$

is obtained, where V_K is the critical molecular volume and A is a constant related with the constants K and C by the equation:

$$A=\frac{C}{K}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

These relations were tested by comparing calculated values with known standard data and the agreement was good for many substances over a wide range of temperatures extending from 0°C. to far above their boiling points.

Recently several reliable data(1) have been added as regards the viscosities and densities of ethyl ether and acetone at low temperatures. The writer is highly indebted to the observers for enabling us to test the above relations also at remarkably low temperatures from 0°C. down to the freezing points.

As will be seen from Figs. 1 and 2, the molecular fluidity Φ of ethyl ether and acetone, calculated from the experimental data and plotted against the molecular surface $V^{\frac{2}{3}}$ or the quantity $(T_K-T)^{\frac{1}{5}}$, gives straight lines except very near the freezing points.

In the case of acetone, the curve of $(\Phi\sim V^{\frac{2}{3}})$ in Fig. 1 falls in two straight lines, respectively referred to the data of Mitsukuri and Tonomura(2) below 0°C. and those of Thorpe and Rodger above it. This is not the case for the temperature relation in Fig. 2, where only one straight line has been obtained. The data of Archibald and Ure deviate from those of the other authors and give slightly curved lines. Such discrepancies may presumably due to the difference of the specimen employed, as is to be seen from the following comparison of density and viscosity of acetone at 0°C. observed by respective author.

Density and viscosity of acetone at 0°C.

Observer	Density	Viscosity
Mitsukuri and Tonomura	0.81392	0.00390
Archibald and Ure	0.81400	0.00389
Thorpe and Rodger	0.81858	0.00394

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(1) Mitsukuri and Tonomura, *J. Chem. Soc. Japan*, **48** (1927), 334; *Proc. Imp. Acad. Japan*, **3** (1927) 155. Archibald and Ure, *J. Chem. Soc.*, **125** (1924), 726; ibid, **128** (1927), 610. Taylor and Smith, *J. Am. Chem. Soc.*, **44** (1922), 2456. Felsing and Durban, ibid, **48** (1926), 2885.

(2) Mitsukuri and Tonomura have also determined the viscosity of methyl alcohol at low temperatures. For this substance the relations (1) and (2) fail as in the case of ethyl alcohol already pointed out in part II. (loc. cit.)

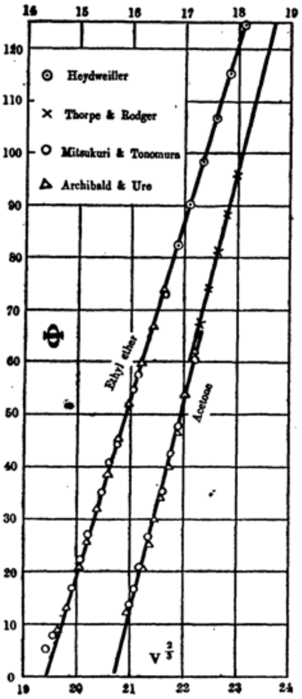

Fig. 1.

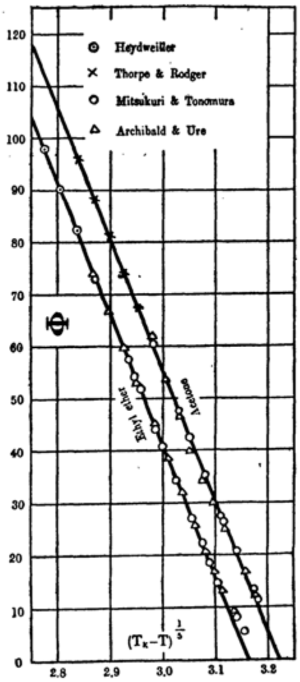

Fig. 2.

In tables 1 and 2, Φ_V gives the molecular fluidity calculated by equation (1) and Φ_T those obtained by equation (2). These values are compared with the experimental data Φ_{obs}.

Table 1.

Ethyl ether.

$$\Phi_V=33.8\ (V^{\frac{2}{3}}-85.69^{\frac{2}{3}}).^{**}$$

$$\Phi_T=791.0-250\ (193.8-t)^{\frac{1}{5}}.$$

$t°C.$	$\Phi_{obs}.$	Φ_V	Δ	Φ_T	Δ
−119.2	5.37	0.2	−52	2.1	−33
−111.7	8.10	3.6	−45	6.0	−21
−109.8	8.98*	6.6	−24	6.9	−21
− 99.8	13.16*	12.1	−11	12.1	−11
− 95.5	14.67	12.7	−20	14.4	− 3
− 92.2	16.81*	15.8	−10	16.1	− 7
− 88.2	18.47	16.9	−16	18.5	0

**These numerical equations have already been obtained from Heydweiller's data between 0° and 100°C. in part II. (loc. cit.)

Table 1. (*Continued.*)

$t°C.$	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−87.7	18.85	17.2	−17	18.7	−2
−84.4	20.78*	20.5	−3	20.5	−3
−80.9	22.25	20.8	−15	22.4	+1
−75.4	25.69*	25.5	−2	25.6	−1
−72.2	27.05	25.5	−16	27.3	+2
−64.5	31.98*	31.8	−2	31.9	−1
−58.9	34.23	33.7	−5	35.2	+10
−58.4	34.95	34.0	−4	35.6	+6
−53.9	38.41*	38.5	+1	38.2	−2
−49.0	40.69	40.1	−6	41.2	+5
−43.0	45.25*	45.3	0	44.9	−4
−42.6	44.25	44.2	−1	45.3	+10
−32.1	52.00*	52.0	0	51.9	−1
−30.1	53.10*	53.4	+3	53.3	+2
−27.5	54.05	54.4	+3	55.0	+9
−26.8	54.87	54.4	−5	55.5	+6
−23.5	57.41	57.4	0	57.7	+3
−20.2	59.71*	60.2	+5	59.9	+2
−10.2	66.71*	67.3	+6	66.9	+2
0.0	73.24	74.6	+14	74.2	+10
0.0	74.08*	74.3	+2	74.2	+1
0	74.40	74.3	−1	74.2	−2
10	82.24	82.4	+2	81.8	−4
20	90.16	89.9	−3	89.7	−5
30	98.42	98.3	−1	97.9	−5
40	106.8	107.3	+5	106.6	−2
50	115.4	116.0	+6	115.9	+5
60	124.6	125.1	+5	125.4	+8
70	135.0	135.3	+3	135.8	+8
80	146.6	145.9	−7	146.9	+3
90	159.1	158.8	−3	158.5	−6
100	172.6	171.8	−8	171.2	−14

Φ_{obs}: 0°—100°C., Heydweiller; * Archibald and Ure; the others, Mitsukuri and Tonomura.

Table 2. Acetone.

$\Phi_V = 41.0\,(V^{\frac{2}{3}} - 62.34^{\frac{2}{3}})$ . . . . Below 0°C.

$\Phi_V = 41.0\,(V^{\frac{2}{3}} - 61.91^{\frac{2}{3}})$ . . . . Above 0°C.

$\Phi_T = 805.3 - 250\,(\overset{**}{23}4.4 - t)^{\frac{1}{5}}$.

$t°C.$	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−92.0	11.68	8.5	−32	9.9	−18
−89.7	12.20*	9.6	−26	11.0	−12
−88.2	13.36	10.2	−32	11.7	−17
−86.7	13.72	11.2	−25	12.4	−13
−79.7	16.57*	14.9	−17	15.9	−7
−79.5	16.78	14.9	−19	15.9	−9

**Galitzine (1890), Landolt-Börnstein-Roth Tabellen, 5 Aufl.

Table 2. (*Continued.*)

$t°C.$	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−71.1	20.67	19.3	−14	20.3	− 4
−69.7	20.68*	20.7	0	21.0	+ 3
−59.7	25.21*	26.1	+ 9	26.2	+10
−59.0	26.55	25.8	− 8	26.6	0
−57.4	27.42	27.0	− 4	27.5	+ 1
−56.9	27.58	27.0	− 6	27.7	+ 1
−49.9	30.11*	31.0	+ 9	31.4	+13
−42.6	35.29	34.9	− 4	35.5	+ 2
−40.0	34.42*	36.4	+20	36.8	+24
−30.2	39.87*	41.8	+19	42.5	+26
−29.7	42.46	42.3	− 2	42.7	+ 2
−29.4	42.42	42.5	+ 1	42.8	+ 4
−20.4	47.08*	47.4	+ 3	48.3	+12
−20.6	47.69	47.7	0	48.2	+ 5
−10.6	53.73*	53.4	+ 3	54.2	+ 5
0.0	62.00*	60.6	−14	60.7	−13
0.0	60.43	60.6	+ 2	60.7	+ 3
0	61.31	61.2	− 1	60.7	− 6
10	67.54	67.6	+ 1	67.2	− 3
20	74.22	73.9	− 3	74.0	− 2
30	81.30	80.8	− 5	80.9	− 4
40	88.43	88.6	+ 2	88.2	− 2
50	96.03	95.9	− 1	95.7	− 3

Φ_{obs}: 0°−50°C., Thorpe and Rodger; * Archibald and Ure; the others, Mitsukuri and Tonomura.

In both cases calculated and observed values stand generally very close to each other except near the freezing points, where calculated values become too small compared with those observed. In this region of tem-

Table 3.

$$\Delta V^{\frac{2}{3}}\% = \frac{V^{\frac{2}{3}} - B^{\frac{2}{3}}}{V^{\frac{2}{3}}} \times 100, \quad \Delta\Phi\% = \frac{\Phi_{obs.} - \Phi_{calc.}}{\Phi_{obs.}} \times 100.$$

$t°C.$	Ethyl ether		Acetone	
	$\Delta V^{\frac{2}{3}}\%$	$\Delta\Phi\%$	$\Delta V^{\frac{2}{3}}\%$	$\Delta\Phi\%$
−120	0	—	—	—
−110	1	−27	—	—
−100	2	− 9	—	—
− 90	3	− 6	1	−23
− 80	3	− 1	2	−11
− 70	4	− 1	3	− 7
− 60	5	− 1	4	− 2
− 50	6	0	5	—
− 40	7	0	5	− 1
− 30	8	0	6	0
− 20	8	+ 1	7	0
− 10	9	+ 1	8	—
± 0	10	0	9	0

peratures the ratio of the molecular free area $(V^{\frac{2}{3}}-B^{\frac{2}{3}})$ to the total surface $V^{\frac{2}{3}}$ becomes very small, as is shown in table 3, so that a slight change in the values of B has a great effect on the magnitude of molecular fluidity. As B is an effective volume of molecules and can hardly be absolutely constant under such a condensed state, it seems rather natural that the deviations from equations (1) and (2) are almost parallel to each other, if it be regarded to have been caused by the change of B.

Table 4. Ethyl ether.

$$V^{\frac{2}{3}}=280.5^{\frac{2}{3}}-7.40\ (193.4-t)^{\frac{1}{5}}.$$

$$\left(A=\frac{C}{K}=\frac{250}{33.8}=7.40\right)$$

t°C.	$V^{\frac{2}{3}}$			V		
	Obs.	Calc.	Δ	Obs.	Calc.	Δ
−120	19.47	19.49	+ 2	85.94	86.04	(+ 10)
−110	19.63	19.64	+ 1	86.96	87.06	(+ 10)
−100	19.79	19.80	+ 1	87.98	88.12	(+ 14)
− 90	19.95	19.95	0	89.02	89.13	(+ 11)
− 80	20.10	20.11	+ 1	90.10	90.18	(+ 8)
− 70	20.28	20.28	0	91.31	91.33	(+ 2)
− 60	20.46	20.45	− 1	92.51	92.49	(− 2)
− 50	20.64	20.64	0	93.69	93.78	(+ 9)
− 40	20.83	20.82	− 1	95.01	95.01	(0)
− 30	21.01	21.01	0	96.34	96.29	(− 5)
− 20	21.21	21.21	0	97.70	97.68	(− 2)
− 10	21.42	21.42	0	99.13	99.06	(− 7)
0	21.63	21.64	+ 1	100.6	100.7	+ 1
+ 10	21.87	21.86	− 1	102.2	102.3	+ 1
20	22.09	22.09	0	103.9	103.8	− 1
30	22.34	22.34	0	105.5	105.6	+ 1
40	22.60	22.59	− 1	107.5	107.4	− 1
50	22.86	22.87	+ 1	109.5	109.4	− 1
60	23.13	23.15	+ 2	111.3	111.4	+ 1
70	23.43	23.46	+ 3	113.4	113.4	0
80	23.74	23.78	+ 4	115.7	116.0	+ 3
90	24.13	24.12	− 1	118.5	118.5	0
100	24.51	24.50	− 1	121.3	121.3	0
110	24.97	24.91	− 6	124.7	124.4	− 3
120	25.47	25.36	− 11	128.5	127.7	− 8
130	26.02	25.86	− 16	132.7	131.5	− 12
140	26.65	26.42	− 23	137.6	135.8	− 18
150	27.35	27.09	− 26	143.1	141.0	− 21
160	28.19	27.89	− 30	149.7	147.2	− 25
170	29.35	28.90	− 45	159.1	155.3	− 38
180	31.12	30.34	− 78	173.6	167.1	− 65
185	32.41	31.42	− 99	184.4	176.1	− 83
190	34.45	33.18	−127	202.2	191.1	−111
192	35.88	34.53	−135	214.8	202.9	−119
193	36.93	35.77	−116	224.5	214.0	−105
193.8	43.03	42.85	− 18	282.2	280.5	− 17

Densities above 0°C. refer to S. Young and below it Taylor and Smith.

This suggests that equation (3), obtained by eliminating the term Φ from equations (1) and (2), would accurately hold even at very low temperatures, and this is really the case as is seen in tables 4 and 5.

At first, the proportionality constant A has been computed from K and C by equation (4) and the constant V_K was then chosen so as to obtain the best agreement with experimental data.

Table 5. Acetone.

$$V^{\frac{2}{3}}=210.2^{\frac{2}{3}}-6.10\,(234.4-t)^{\frac{1}{5}}.$$

$$\left(A=\frac{C}{K}=\frac{250}{41.0}=6.10\right)$$

$t°C.$	$V^{\frac{2}{3}}$		Δ	V		Δ
	Obs.	Calc.		Obs.	Calc.	
−90	15.94	15.98	+ 4	63.75	63.89	+14
−80	16.08	16.09	+ 1	64.49	64.54	+ 5
−70	16.18	16.21	+ 3	65.25	65.27	+ 2
−60	16.34	16.34	0	66.04	66.07	+ 3
−50	16.47	16.47	0	66.85	66.82	− 3
−40	16.61	16.61	0	67.69	67.70	+ 1
−30	16.75	16.74	− 1	68.55	68.50	− 5
−20	16.90	16.89	− 1	69.44	69.44	0
−10	17.05	17.04	− 1	70.39	70.33	− 6
0	17.20	17.19	− 1	71.32	71.25	− 7
+10	17.36	17.35	− 1	72.30	72.24	− 6
20	17.52	17.52	0	73.31	73.33	+ 2
30	17.68	17.68	0	74.37	74.35	− 2
40	17.85	17.86	+ 1	75.46	75.50	+ 4
50	18.03	18.04	+ 1	76.60	76.61	+ 1

The agreement between calculated and observed values is very good even down to the freezing points, except that very near the critical temperatures a deviation of about 1 to 5% appears.

In part IV of this paper, it has been shown that B is an additive constant and K, B, C and Φ_K in equations (1) and (2) take universal values when they are expressed in reduced form. Since such calculations have been already given for ethyl ether, only the result for acetone is shown in the following:

$$B_{obs.}=62.3\sim61.9 \qquad B_{calc.}=61.8.$$

$$b_R=\frac{B}{V_K}=0.297\sim0.295\ (0.308).$$

$$k_R=\frac{KV_K^{\frac{2}{3}}}{\Phi_K}1.80\sim1.79\ (1.84).$$

$$k'_R=K.M.^{\frac{1}{2}}T_K{}^{\frac{1}{2}}V_K{}^{\frac{1}{3}}=4.18\times10^4\ (4.03\times10^4).$$

$$c_R=\frac{CT_K{}^{\frac{1}{5}}}{\Phi_K}=1.08\ (1.09).$$

$$c'_R=\frac{CM^{\frac{1}{2}}\,T_K{}^{\frac{7}{10}}}{V^{\frac{1}{3}}{}_K}=2.51\times10^4\ (2.40\times10^4).$$

$$\phi'_R=\frac{\Phi_K M^{\frac{1}{2}}\,T_K{}^{\frac{1}{2}}}{V_K{}^{\frac{1}{3}}}=2.32\times10^4\ (2.19\times10^4).$$

The mean values obtained as the average for many substances are shown in parentheses. From the above result it may be concluded that the reduced equations cited in Part IV would also hold fairly good for acetone without any change.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

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