THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART II.(1)

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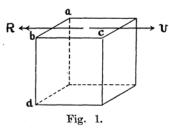
Relation between Viscosity and Volume or Temperature.

1. Definition of Molecular and Specific Fluidity. The coefficient of viscosity η is defined by the formula:

$$R = \eta \cdot \frac{dv}{dz} \cdot A.$$

where R is tangential resistance, $\frac{dv}{dz}$ velocity gradient along the normal and

A area. Therefore, it may also be defined as follows: we consider at first



an unit cube (Fig. 1.) filled with a viscous substance. The viscosity of the substance is measured by the tangential resistance R on the upper plane of the cube, when it moves with unit velocity in respect to the lower.

In order to express the viscosity in a molecular term, Thorpe and Rodger⁽²⁾ proposed the molecular viscosity, which is defined

by the product $\eta \cdot V^{\frac{3}{3}}$, V being molecular volume, so that the molecular viscosity after Thorpe and Rodger is equal to the resistance when the sliding surface contains equal number of molecules, i.e. when in Fig. 1. $ab = bc = V^{\frac{1}{3}}$ while bd = 1. The conception of this quantity seems not to be adequate, since, although equal number of molecules are arranged for different substances along ab and bc, it is not so in the direction bd. The expression $\eta \cdot V^{\frac{2}{3}}$ may strictly be called molecular surface viscosity. The true molecular viscosity should be defined as follows: the molecular viscosity is measured by the resistance when the same number of molecules are arranged also in the direction of normal bd, i.e. when $ab = bc = bd = V^{\frac{1}{3}}$ in Fig. 1. Putting $ab = bc = bd = V^{\frac{1}{3}}$ where V_1 is specific volume, specific viscosity may similarly be defined.

⁽¹⁾ Part I, This Journal, 2 (1927), 95.

⁽²⁾ Thorpe and Rodger, Phil. Trans., (A), 185 (1894), 397.

162 T. Titani.

As the term of molecular viscosity are already conventionally understood in the sense of Thorpe and Rodger, the writer proposes to introduce the new proper definition for molecular and specific fluidity as the reciprocal of the above two quantities.

The coefficient of fluidity, denoted by ϕ , is the reciprocal of the coefficient of viscosity, so that it may be defined as the velocity v given to the upper plane referred to the lower (Fig. 1), by unit tangential force applied to the upper plane. Consequently, molecular fluidity ϕ is measured by the sliding velocity given by unit tangential force applied to a plane containing the same number of molecules for different substances, the velocity being referred to another fixed plane, the distance between the two planes also having the same number of molecules. In Fig. 1., when $ab=bc=bd=V^{\frac{1}{3}}$, the velocity v measures molecular fluidity ϕ . Specific fluidity ϕ_1 is similarly defined as the velocity v in Fig. 1. when $ab=bc=bd=V^{\frac{1}{3}}$.

These two quantities can be calculated from the value of viscosity η or fluidity ϕ and molecular V or specific volume V_1 from the following relations:

$$\Phi = \frac{\phi}{V^{\frac{1}{3}}} = \frac{1}{\eta \cdot V^{\frac{1}{3}}}....(1)$$

$$\Phi_1 = \frac{\phi}{V_1^{\frac{1}{3}}} = \frac{1}{\eta \cdot V_1^{\frac{1}{3}}}....(2)$$

2. Relation between Molecular Fluidity and Molecular Volume. As the relation between viscosity η and specific volume V_1 , Batschinski⁽¹⁾ put forward the following experimental formula:

$$\eta = \frac{c}{(V_1 - \omega)} \qquad (3)$$

where c and ω are constants. This relation seems to have little theoretical lucidity, since viscosity in the left side is referred to unit cube, while specific volume in the right side being referred to one gram.

We will consider the molecular fluidity defined above as regards its relation to the molecular volume. Suppose the upper plane of the cube in Fig. 1 is displaced in reference to the lower by the amount du during the time $d\theta$ by unit tangential force applied to the upper plane. Then the displacement du measures the amount of shear of the vertical side. Therefore it seems plausible to assume this displacement to be proportional to the free space in the plane cbd, i.e. the area of the plane decreased by the amount proportional to the section of molecules:

⁽¹⁾ Batschinski, Z. physik. Chem., 84 (1913), 643.

$$du = K. (V^{\frac{2}{3}} - B^{\frac{2}{3}}). d\theta.$$

where K and B are constants. Dividing both sides with $d\theta$ and taking into consideration that $\frac{du}{d\theta}$ is equal to molecular fluidity φ , the above relation becomes,

$$\Phi = K. (V^{\frac{2}{3}} - B^{\frac{2}{3}}) \dots (4)$$

The constant B is the limiting value of the molecular volume of liquid as its molecular fluidity approaches zero, and it is therefore called effective molecular volume. Calling the difference $(V^{\frac{2}{3}} - B^{\frac{2}{3}})$ the molecular free area, the above relation may be expressed as follows: the molecular fluidity varies directly as the molecular free area.

Similarly, for the specific fluidity we obtain the following relation:

were K_1 and B_1 are constants having similar meanings as K and B and being related with them by the equations:

$$K_1 = M. K$$
, and $B_1 = \frac{B}{M}$.

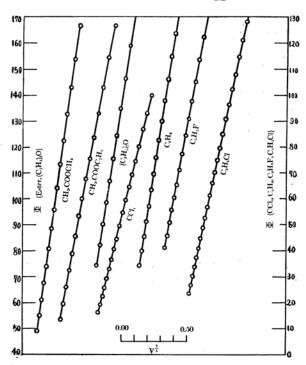


Fig. 2.—The volume relation for organic liquids extended over boiling points.

164 T. Titani.

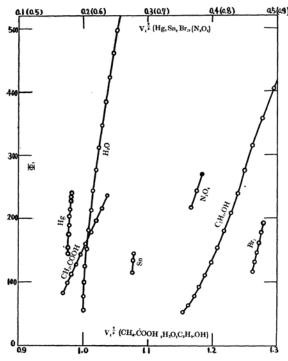


Fig. 3.—The volume relation for abnormal and inorganic liquids.

where *M* being the molecular weight. The above two relations (4) and (5) will be called the volume relation. This is graphically summarised in Figs. 2. and 3., the details of numerical data are given in later tables. The volume relation is found to be satisfied by many substances. The calculated values of molenular or specific fluidity seldom deviate from the observed values by more than one per cent. Few substances for which the agreement is not good include alcohols, water and mercury, so long as being tested.

Multiplying both sides of the equation (5) with $V_1^{\frac{1}{3}}$ and inverting it, we have:

$$\eta = \frac{\frac{1}{K_1}}{(V_1 - B_1^{\frac{2}{3}} \cdot V_1^{\frac{1}{3}})}....(6)$$

Comparing this expression with that of Batschinski (3), we see that a constant ω in the latter corresponds to a variable $B_1^{\frac{2}{3}}$. $V_1^{\frac{1}{3}}$ in the former (6).

⁽¹⁾ Although the definition of molecular or specific fluidity and their relation to volume need the data of density, this is not accompanied by introduction of a new unknown quantity, since the value of density is always necessary for the measurement of viscosity.

The effect due to this difference in formula may not be large until a comparison is done over a wide temperature range up to the critical point, but in this case a remarkable difference would appear between the values calculated by each equation.

3. Relation between Molecular Fluidity and Temperature. Viscosity or fluidity is one of the properties which change most remarkably with temperature, and as regards their variation with temperature, so many equations have been proposed that one can hardly decide which one is to be preferred.

If the volume relation obtained above be correct from the freezing point up to the critical, the molecular fluidity would approach zero at a certain low temperature, while near the critical it would increase very rapidly to a certain critical value. As one of the formula satisfying these conditions and containing constants as few as possible, the following relation is proposed:

$$\log\left(\varPhi_{\kappa}-\varPhi\right)=\frac{1}{5}\log\left(T_{\kappa}-T\right)+\mathrm{Const.}$$

 \cdot or

$$(\Phi_K - \Phi) = C.(T_K - T)^{\frac{1}{5}}....(7)$$

where T_K is critical temperature, Φ_K the value of molecular fluidity at this point, C a constant. Similarly, for the specific fluidity:

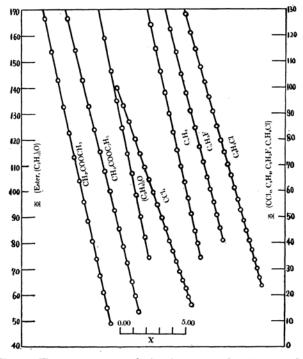


Fig. 4.—The temperature relation for organic liquids extended over boiling points.

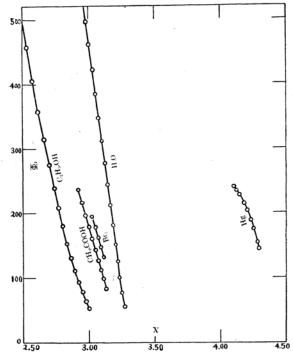


Fig. 5.—The temperature relation for abnormal and inorganic liquids.

$$(\Phi_{1K} - \Phi_1) = C_1 \cdot (T_K - T)^{\frac{1}{5}} \cdot \dots (8)$$

where respective quantities are each referred to one gram and—

$$C_1 = M^{\frac{1}{3}}. C.$$
 $\Phi_{1K} = M^{\frac{1}{3}}. \Phi_{K}.$

M being the molecular weight. These relations will be called temperature relation. The temperature relation was found to be satisfied by many substances with a few exceptions (alcohols, water and mercury so long as being tested) as being shown graphically in Figs. 4. and 5. and numerically in later tables.

Notation:—t: Temperature in Celcius degree.

Φ: Molecular fluidity observed.

 Φ_{ν} : Molecular fluidity calculated from volume.

 Φ_T : Molecular fluidity calculated from temperature.

Constants K, C etc. were determined graphically. Most of the necessary data were taken from the papers of S. Young, (1) Thorpe and Rodger, (2)-

¹⁾ Density: S. Young, Sci. Proc. Roy. Dublin Soc., 12 (1909-1910), 374.

²⁾ Viscosity: Thorpe & Rodger, Fhil. Trans., (A), 185 (1894), 397; ibid., 189 (1897), 71.

A. Heydweiller⁽¹⁾ and the writer's own.⁽²⁾ A few others were from the Tables of Landolt-Börnstein-Roth, 5 edition.

Normal Pentane. $\varphi_{\nu} = 31.8 \; (V^{\frac{2}{3}} - 95.50^{\frac{2}{3}}).$ $\varphi_{T} = 795.4 - 251 \; (197.2 - t)^{\frac{1}{5}}.$

t	Φ	Φ_V	Φ_T
0	73.36	73.5	73.5
10	80.87	80.7	80.7
20	88.59	88.7	88.5
30	96.47	96.4	96.7

t	Φ	Φ_V	Φ_T
0	75.82	75.8	75.9
10	83.71	83.7	83.7
20	91.85	91.7	91.9
30	99.86	100.3	99.7

t	Ф	Φ_V	Φ_T
0	50.16	50.3	50.2
	55.77	55.9	55.7
20	61.60	61.6	61.7
30	67.63	67.7	67.7
40	73.98	73.8	74.1
50	80.63	80.5	80.7
60	87.46	87.7	87.5

t	ф	$\Phi \nu$	Φ_T
0	36.84	36.8	36.5
10	41.40	41.4	41.4
20	46.20	45.9	46.2

Normal Heptane. (continued)

30	51.21	51.5	51.3
40	56.32	56.5	56.4
50	61.81	62.2	61.9
60	67.54	67.4	67.4
70	73.37	73.3	73.3
80	79.62	79.5	79.5
90	85.90	85.3	86.3

t	Φ	Φ_V	Φ_{T}
0	26.26	25.8	26.1
10	30.02	29.7	30.1
20	34.06	34.1	34.3
30	38.15	38.5	38.5
40	42.48	42.5	42.8
50	46.97	47.2	47.3
60	51.60 56.48	52.0 56.7	51.9
70 80	61.56	61.8	$ \begin{array}{c} 56.9 \\ 62.0 \end{array} $
90	66.92	66.9	67.3
100	72.46	72.7	72.5
110	78.18	78.3	78.1
120	84.57	84.0	84.0

$$\begin{split} &\text{Methyl-formate.}\\ &\varPhi_V \!=\! 43.8 \ (\textit{V}^{\frac{2}{3}}\!-\!52.04^{\frac{2}{3}}).\\ &\varPhi_T \!=\! 729.5\!-\!229 \ (214.0\!-\!t)^{\frac{1}{5}}. \end{split}$$

t	Ф	Φ_V	Φ_T
0	59.60	59.7	59.8
10	66.27	66.3	66.2
20	72.98	72.7	72.8
30	79.47	79.7	79.7

$$\begin{split} & \text{Ethyl-formate.} \\ \mathscr{O}_{V} = & 34.0 \; (V^{\frac{3}{3}} - 69.60^{\frac{2}{3}}). \\ \mathscr{O}_{T} = & 696.1 - 218 \; (235.3 - t)^{\frac{1}{5}}. \end{split}$$

- Viscosity above boiling points: A. Heydweiller, Wied. Ann., 55 (1895), 561; ibid., 59 (1896), 198.
- (2) Viscosity above boiling points: the writer, this paper part I. (loc. cit.)

Ethyl-formate. (continued)

t	Ф	ΦV	Φ_T
0	46.32	46.2	46.3
10	51.96	52.2	51.8
20	57.66	57.7	57.7
30	63.72	63.9	63.7
40	70.00	69.8	70.0
50	76.28	76.3	76.6

t	Ф	Φ_V	Φ_T
0 10	32.83	32.9	32.7
	37.40	37.3	37.4
20	42.17	42.3	42.4
30	47.19	47.2	47.4
40	52.47	52.5	52.5
50	57.85	57.9	58.0
60 70	63.50	63.5	63.6
	69.37	69.3	69.4
80	75.54	75.5	75.5

$$\begin{split} &\text{Methyl-acetate.} \\ & \varPsi_{V} \! = \! 37.1 \; (\, V^{\frac{2}{3}} \! - \! 68.93^{\frac{2}{3}}). \\ & \varPsi_{T} \! = \! 742.4 \! - \! 233 \; (233.7 \! - \! t)^{\frac{1}{5}}. \end{split}$$

t	Φ	Φ_{V}	Φ_T
0	49.14	48.9	48.8
10	5 5 .00	54.8	54.8
20	61.09	61.1	61.0
30	67.35	67.4	67.6
40	73.89	74.2	74.4
50	80.78	81.3	81.4
60	88.47	88.5	88.8
70	95.81	96.0	96.4
80	104.0	104.4	104.6
90	113.3	112.5	113.0
100	122.6	121.7	122.1
110	132.7	131.7	131.6
120	142.9	I42.3	141.9
130	153.8	153.9	152.9
140	166.6	166.6	164.7
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Ethyl-acetate. (continued)

t	Φ	Φ_{V}	Φ_T
30	53.53	54.1	53.9
40	59.73	59.7	59.5
50	66.03	65.7	65.6
60	72.41	71.7	71.7
70	78 83	78.8	78.2
80	85.59	85.0	85.1
90	92.68	92.0	92.0
100	100.1	99.1	99.5
110	107.7	107.1	107.4
120	115.5	115.5	115.8
130	123.8	124.4	124.6
140	132.9	133.4	134.0
150	143.1	144.6	144.2
160	154.5	155.9	155.4
170	166.7	168.7	167.4
180	179.9	182.3	180.7

$$\begin{split} & \text{Propyl-acetate.} \\ & \varPsi_{r} \!=\! 23.8 \; (V^{\frac{2}{3}} \!-\! 104.2^{\frac{2}{3}}). \\ & \varPsi_{T} \!=\! 630.0 \!-\! 196 \; (276.2 \!-\! t)^{\frac{1}{5}}. \end{split}$$

t	Φ	Φ_V	Φ_T
0	26.93	23.7	23.7
10 20	$\frac{31.04}{35.40}$	31.0 35.4	$\frac{31.2}{35.7}$
30	40.09	40.2	40.4
40	44.83	45.0	45.2
50 60	$\frac{49.77}{55.00}$	50.1 55.4	50.3 55.5
70	60.36	60.8	60.8
80	66.00	66.4	66.7
90 100	72.19 79.30	$72.6 \\ 78.6$	$\frac{72.4}{78.6}$

$$\begin{split} &\text{Methyl-propionate.} \\ & \varPhi_V \!=\! 28.9 \; (V^{\frac{2}{3}} \!-\! 85.04^{\frac{2}{3}}). \\ & \varPhi_T \!=\! 669.2 \!-\! 208 \; (257.4 \!-\! t)^{\frac{1}{5}}. \end{split}$$

t	Φ	Φ_V	Φ_T
0	37.82	37.8	37.9
$\frac{10}{20}$	42.80	43.0	42.9
	48.06	47.9	48.0
30	53.26	53.0	53.3
	58.79	58.7	58.9
60	70.49	70.5	70.5
50	64.46	64.7	64.6
60	70.49	70.5	70.5
70	76.85	76.5	76.8

Ethyl-propionate.

(continued)

Ethyl-ether. (continued)

	t	Ф	Φ_V	Φ_T
	0	29.94	29.8	29.8
	10	34.22	34.3	34.2
	20	38.69	38.6	38.9
	30	43.43	43.3	43.6
	40	48.30	48.4	48.6
1	50	53.37	53.7	53.6
ĺ	60	58.60	58.9	58.8
	70	64.19	64.2	64.2
	80	70.01	69.9	69.9
1	90	76.05	76.0	75.8
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t	Φ	Φ_V	Φ_{T}
0	74.40	74.3	74.2
10	82.24	82.4	81.8
20	90.16	89.9	89.7
30 40	98.42 106.8	98.3 107.3	97.9 106.6
50	115.4	116.0	115.9
60	124.6	125.1	125.4
70	135.0	135.3	135.8
80	146.6	145.9	146.9
90	159.1	158.8	158.5
100	172.6	171.8	171.2

$$\begin{split} & \text{Methyl-butyrate.} \\ & \varPhi_{\mathcal{V}} \!=\! 23.6 \; (\textit{V}^{\frac{2}{3}} \!-\! 102.7^{\frac{2}{3}}). \\ & \varPhi_{\mathcal{T}} \!=\! 623.5 \!-\! 193 \; (281.3 \!-\! t)^{\frac{1}{5}}. \end{split}$$

t	Φ	$\Phi_{\mathcal{V}}$	$\Phi_{\boldsymbol{T}}$
0	27.43	27.4	27.3
10	31.55	31.9	31.5
20	35.91	36.0	36.0
30	40.48	40.6	40.6
40	45.20	45.5	45.3
50	50.08	50.4	50.2
60	55.22	55.4	55.2
70	60.50	60.5	60.4
80	66.16	65.8	65.8
90	72.01	71.4	71.5
100	77.82	77.2	77.3

$$\begin{split} &\text{Carbon-tetrachloride.} \\ & \varPsi_{V} \!=\! 20.4 \; (\,V^{\frac{2}{3}} \!-\! 88.88^{\frac{2}{3}}). \\ & \varPsi_{T} \!=\! 470.7 \!-\! 147 \; (283.15 \!-\! t)^{\frac{1}{5}}. \end{split}$$

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	Φ	Φ_{V}	Φ_T
0	16.31	16.1	16.1
10	19.32	19.5	19.3
20	22.50	22.6	22.6
30	25.75	26.4	25.1
40	29.27	29.6	29.6
50	33.08	33.6	33.3
60	36.65	37.3	37.2
70	40.74	41.4	41.1
80	45.41	45.3	45.2
90	49.65	49.7	49.5
100	54.82	54.2	53.9
110	59.50	58.6	58.6
120	64.49	63.8	63.7
130	69.29	68.8	68.5
140	74.64	74.3	73.9
150	80.33	79.9	79.7
160	87.02	85.5	85.7
170	93.22	92.1	92.2
180	100.0	98.6	99.2
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 $\begin{aligned} &\text{Methyl-isobutyrate.}\\ & \varPhi_{V} \!=\! 23.8 \ (V^{\frac{2}{3}} \!-\! 102.9^{\frac{2}{3}}).\\ & \varPhi_{T} \!=\! 624.0 \!-\! 194 \ (267.55 \!-\! t)^{\frac{1}{5}}. \end{aligned}$

t	Ф	Φ_V	Φ_T
0	30.84	30.6	30.7
10	35.20	35.2	35.2
20	39.72	39.8	39.8
30	44.43	44.7	44.6
40	49.38	49.8	49.6
50	54.59	54.8	54.7
60	59.89	60.1	60.0
70	65.54	65.5	65.5
80	71.48	71.5	71.4
90	77.82	77.3	77.3

t	Φ	Φ_{V}	Φ_{T}
20	34.62	34.3	34.3
30	39.92	39.7	39.8
40	45.47	45.8	45.4
50	51.18	51.6	51.3
60	57.18	57.7	57.3
70	63.37	63.3	63.5
80	69.58	69.9	70.0
90	75.95	75.3	75.6
100	82.75	83.3	83.6

Benzene.

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110	90.10	90.4	91.0
120	97.95	98.0	97.6
130	106.3	106.0	106.6
140	115.1	114 9	115.0
150	124.3	124.0	123.9
160	134.1	132.9	133.3
170	144.6	143.4	143.2
170	144.6	143.4	143.2
	156.4	153.7	154.0

Fluorobenzene.

$$\begin{split} & \varPhi_V \!=\! 28.8 \; (\,V^{\frac{2}{3}} \!-\! 85.51^{\frac{2}{3}}). \\ & \varPhi_T \!=\! 647.3 \!-\! 200 \; (286.55 \!-\! t)^{\frac{1}{5}}. \end{split}$$

t	Φ	Φ_{V}	Φ_{T}
30	41.19	40.9	40.9
40	45.66	45.6	45.6
50	50.81	50.3	50.5
60	55.71	55.5	£5.6
70	60.38	60.8	61.1
80	65.25	65.9	66.5
90	71.22	72.1	72.3
100	77.32	78.2	78.1
110	84.45	84.4	84.5
120	91.11	91.2	91.0
130	97.81	93.4	97.8
140	105.2	105.7	105.0
150	113.7	113.4	112.6
160	122.4	122.8	120.7
170	131.0	130.4	129.2
180	141.0	139.6	138.4

Chlorobenzene.

t	Φ	$\Phi_{\mathcal{V}}$	$\Phi_{m{T}}$
10	23.70	23.6	23.6
20	26.81	27.0	27.0
30	30.29	30.5	30.4
40	33.66	34.0	34.0
50	37.42	37.5	37.5
60	41.06	41.2	41.2
70	44.74	45.0	45.1
80	48.72	48.8	48.9
90	52.70	53.0	53.0
100	56.80	56.8	57.0
110	61.27	61.2	61.3
120	65.10	65.7	65.6
130	70.31	70.5	70.3
140	74.89	75.1	75.0
150	79.74	79.8	79.9
160	85.13	84.9	84.7
170	90.84	90.2	90.2
180	96.49	95.8	95.7
190	102.3	101.6	101.5
200	107.9	107.8	107.6
210	114.8	114.4	113.9
220	121.2	120.9	120.7
230	128.3	128.5	127.7
240	135.5	136.8	135.3

For the following substances quantities are all referred to one gram and this is meant by the index 1 under the symbol.

Acetic acid.
$$\varPhi_{1\nu}\!=\!2250~(~{V_1}^{\frac{2}{3}}\!-\!0.8997^{\frac{2}{3}}).$$

$$\Phi_{1T} = 2291 - 705 (321.6 - t)^{\frac{1}{5}}.$$

t	Φ_1	Φ_{1}_{V}	Φ_{1T}
20	83.32	83	82
30	97.74	96	97
40	112.0	112	113
50	127.2	127	128
60	143.1	144	144
70	159.7	160	162
80	177.6	178	178
90	196.2	196	197
100	215.7	215	215
110	235.8	234	234

Bromine.

Φ_1	$\Phi_1 \nu$	Φ1Τ
117.0	117	117
132.3	132	132
147.1	147	147
162.0	161	161
177.5	177	178
193.6	194	194
	117.0 132.3 147.1 162.0 177.5	117.0 117 132.3 132 147.1 147 162.0 161 177.5 177

Nitrogen peroxide. $\varphi_{1V} = 3250 \ (V_1^{\frac{2}{3}} - 0.5855^{\frac{2}{3}}).$

t	Фі	Φ_{1V}
0	216.6	217
10	242.9	243
20	270.4	270

Molten Tin. $\varphi_{1\nu} = 16000 \ (V_1^{\frac{2}{3}} - 0.1247^{\frac{2}{3}}).$

(t)	Φ_1	$\Phi_1_{\mathcal{V}}$
280	113.8 (110.4?)	111
296	114.7	115
357	134.0	134
389	145.1	144

?: Extrapolated from the other temperatures.

From above results, it may be concluded that equations (4), (7), etc. expressing the relations among molecular fluidity $(^1/_{\eta}, V^{\frac{1}{3}})$, molecular volume and absolute temperature hold good for most substances except a few which include alcohols, water and mercury.

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

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