# THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS.
## PART. III.

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Received June 1, 1927. Published July 28, 1927.

**1. Specific Fluidity of Liquid Carbon dioxide.** P. Phillips(2) determined the viscosity of carbon dioxide at several temperatures under high pressures. Calculating the specific fluidity $\Phi_1$ from his data and plotting it against the specific surface $V_1^{\frac{2}{3}}$, every point falls almost on a straight line as will be seen from Fig. 1. In the table below, the observed values of specific fluidity are compared with those calculated from the equation(3)

$$\Phi_1 = K_1 (V_1^{\frac{2}{3}} - B_1^{\frac{2}{3}}) \cdots\cdots\cdots\cdots (1).$$

where $K_1 = 3060, \quad B_1 = 0.669.$

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(2) P. Phillips, *Proc. Roy. Soc.*, (A), 87, (1912), 48.

(3) Cf. Part II of this paper, this journal, 2 (1927), 161.

## TABLE 1.

## Liquid Carbon dioxide.

20° C.

| Pressure Atm. | $\Phi_1 \times 10^{-1}$ | |
|---|---|---|
| | Observed | Calculated |
| 83 | 114.4 | 111 |
| 72 | 121.0 | 118 |
| 59 | 131.4 | 131 |

30° C.

| Pressure Atm. | $\Phi_1 \times 10^{-1}$ Observed | $\Phi_1 \times 10^{-1}$ Calculated |
|---|---|---|
| 110.5 | 120.3 | 123 |
| 104 | 125.6 | 127 |
| 96 | 131.6 | 134 |
| 90 | 140.8 | 139 |
| 82 | 151.1 | 148 |
| 80 | 157.7 | 152 |
| 76 | 166.2 | 162 |
| 74 | 176.2 | 168 |
| 73 | 181.5 | 172 |
| 72 | 187.6 | 180 |

32° C.

| Pressure Atm. | $\Phi_1 \times 10^{-1}$. | |
|---|---|---|
| | Observed. | Calculated. |
| 120 | 117.3 | 124 |
| 112 | 124.1 | 128 |
| 104 | 131.3 | 133 |
| 93 | 143.5 | 144 |
| 87 | 151.5 | 154 |
| 84 | 157.2 | 161 |
| 80 | 164.4 | 172 |
| 76 | 196.3 | 197 |

35° C.

| Pressure Atm. | $\Phi_1 \times 10^{-1}$ Observed. | $\Phi_1 \times 10^{-1}$ Calculated. |
|---|---|---|
| 114.5 | 131.4 | 135 |
| 109 | 137.1 | 140 |
| 96 | 151.2 | 156 |
| 88 | 169.8 | 172 |
| 85 | 187.6 | 184 |

40° C.

| Pressure Atm. | $\Phi_1 \times 10^{-1}$ Observed. | $\Phi_1 \times 10^{-1}$ Calculated. |
|---|---|---|
| 112 | 155.3 | 155 |
| 108 | 163.0 | 161 |
| 100 | 178.0 | 180 |
| 94 | 201.7 | 205 |

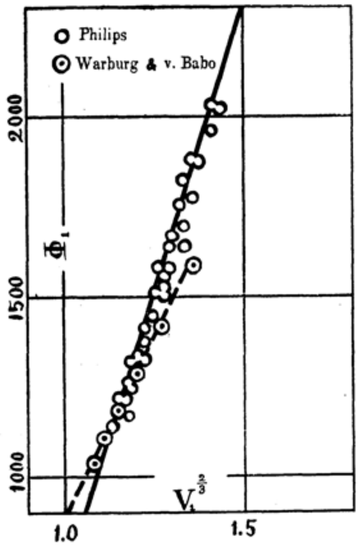

Fig. 1:—Volume Relation for Liquid Carbon dioxide.

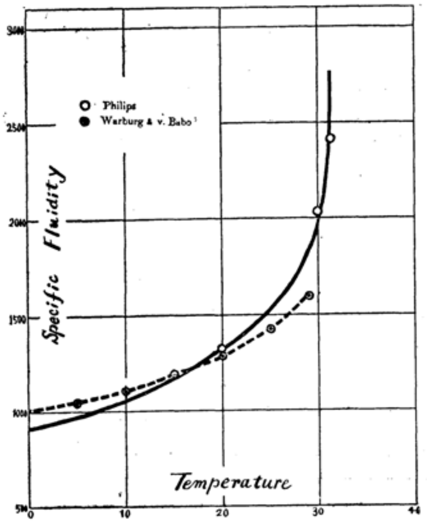

Fig. 2:—Orthobaric Specific.Fluidity of Liquid Carbon dioxide.

The specific fluidity for orthobaric volume(1) was found from equation (1) and, plotting it against the temperature, a full curve shown in Fig. 2 was obtained. The two observed (at 20° and 30°) and one estimated value (at critical point 31.°35) of P. Phillips, shown by circles, fall almost on the curve.

The viscosity of carbon dioxide under orthobaric state were early determined by Warburg and v. Babo.(2) Using their data, we have the dotted lines shown in Figs. 1 and 2. A remarkable discrepancy between the observed values of respective authors may probably be due to difference of specimen employed.

2. **Comparison of Volume and Temperature Relations of Molecular Fluidity.** In part II(3) of this paper we obtained as a relation between molecular volume $V$ and molecular fluidity $\Phi$:

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

where $K$ and $B$ are constants, and as its relation to temperature $T$:

$$\Phi = \Phi_k - C\,(T_k - T)^{\frac{1}{3}} \cdots\cdots (3).$$

were $\Phi_k$ and $T_k$ are critical and $C$ an arbitrary constant. The same form of relations hold also with specific fluidity.

(A). Putting $\Phi = 0$ in equation (3), we have the temperature $t_s$, where viscosity becomes infinity. This temperature $t_s$ is found to be very near the freezing point $t_F$ for many substances except a few. (see Table 2, column 2 and 3). Exact agreement between calculated and observed freezing point can not be expected, since $t_s$ is to be a solidifying temperature of a substance, regarding it as quite isotropic.

(B). $T_s$ is almost equal to $\frac{7}{20}$ of the critical temperature $T_k$, both being measured in absolute scale. (see Table 2, column 4).

(C). The term $B$ in equation (2) represents the molecular volume when viscosity becomes infinity. Therefore, this should be the molecular volume $V_s$ at the temperature $t_s$. In order to compute the density at the temperature $t_s$ the rule of Cailletet and Mathias modified by S. Young(4) was used. The agreement between $B$ and $V_s$ is very satisfactory, the difference being all far less than 1%, as will be seen from the columns 5 and 6 in Table 2.

(D). The critical value of molecular fluidity $\Phi_{kT}$ in equation (3) is compared with $\Phi_{kv}$ found from equation (2) by putting critical volume in it. (see Table 2, columns 7 and 8). The agreement between two sorts of $\Phi_k$ is

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(1) Amagat, *Compt. rend.*, **114** (1892) 1093.

(2) Warburg & v. Babo, *Wied. Ann.*, **17** (1882), 390.

(3) loc. cit.

(4) S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1909—1910), 374.

satisfactory, if it be taken into account that the magnitude of these quantities is remarkably effected by a slight change in the values of other constants.

TABLE 2.

| Substance. | $t_F$ | $t_s$ | $\frac{T_s}{T_k}$ | $B$ | $V_s$ | $\Phi_{kv}$ | $\Phi_{kT}$ |
|---|---|---|---|---|---|---|---|
| Pentane. | −130.8° | −122.4° | 0.321 | 95.5 | 95.0 | 796 | 795 |
| Isopentane. | −158.05 | −121.2 | 0.330 | 96.1 | 95.5 | 790 | 800 |
| Hexane. | − 94.3 | −105.2 | 0.331 | 112.6 | 111.6 | 710 | 703 |
| Heptane. | − 90.0 | − 89.6 | 0.340 | 129.9 | 129.1 | 674 | 660 |
| Octane. | − 56.5 | − 71.9 | 0.353 | 147.9 | 147.3 | 637 | 613 |
| Methyl-formate. | − 99.75 | −114.1 | 0.326 | 52.0 | 51.7 | 745 | 730 |
| Ethyl-formate. | − 80.5 | − 96.6 | 0.347 | 69.6 | 70.0 | 699 | 696 |
| Propyl-formate. | . . | − 77.9 | 0.363 | 86.8 | 86.5 | 651 | 649 |
| Methyl-acetate. | − 98.05 | − 94.8 | 0.351 | 68.9 | 68.7 | 760 | 742 |
| Ethyl-acetate. | − 83.4 | − 83.7 | 0.362 | 86.1 | 86.0 | 675 | 674 |
| Propyl-acetate. | . . | − 66.6 | 0.376 | 104.2 | 104.0 | 644 | 630 |
| Methyl-propionate. | . . | − 88.5 | 0.348 | 85.0 | 84.5 | 684 | 669 |
| Ethyl-propionate. | − 73.9 | − 75.4 | 0.362 | 102.9 | 102.4 | 638 | 628 |
| Methyl-butyrate. | . . | − 70.7 | 0.365 | 102.7 | 102.5 | 631 | 624 |
| Methyl-isobutyrate. | . . | − 76.7 | 0.363 | 102.9 | 102.4 | 634 | 624 |
| Ethyl-ether. | −116.2 | −123.6 | 0.320 | 85.7 | 85.3 | 797 | 791 |
| Carbon-tetrachloride. | − 22.95 | − 53.3 | 0.395 | 88.9 | 88.6 | 459 | 471 |
| Benzene. | 5.484 | − 50.0 | 0.397 | 82.2 | 81.9 | 737 | 757 |
| Fluorobenzene. | − 41.2 | − 68.6 | 0.365 | 85.5 | 85.0 | 648 | 647 |
| Chlorobenzene. | − 45 | − 67.9 | 0.325 | 94.1 | 93.7 | 611 | 601 |
| Acetic acid. | 16.67 | − 40.6 | 0.391 | (0.900) | (0.898) | (2428) | (2291) |
| Bromine. | − 7.3 | − 91.4 | 0.316 | (0.287) | (0.289) | (2027) | (2273) |

Note:—Numbers in brackets represent the quantities referred to one gram,

(E) The comparison of the two sorts of relations, (2) and (3), was done over a wide range of temperature. The result for ethyl ether is given in Fig. 3, as an example, where the following numerical equations(1) already obtained have been used.

$$\Phi_v = 33.8\,(V^{\frac{2}{3}} - 85.69^{\frac{2}{5}}).\cdots\cdots\cdots(4).$$

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

Equation (4) is given in full line and equation (5) in dotted. The agreement between the two is generally good, except near the critical tempereture. In this region errors of calculation becomes very large, since the term $(T_k - T)^{\frac{1}{5}}$ in equation (3) becomes very small and volume in equation (2) changes rapidly.

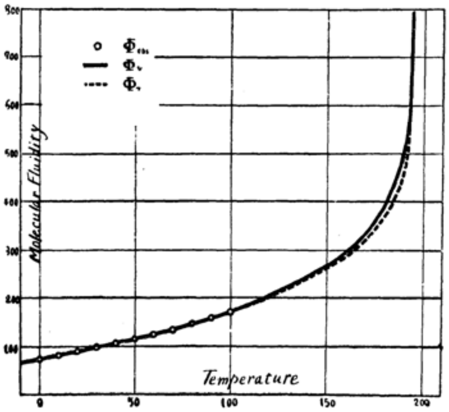

Fig. 3:—Comparison of Volume and Temperature Relations with Ethyl ether.

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(1) Part II. of this paper cited above.

**3. Relation between Orthobaric Volume and Temperature.** At low temperatures the orthonaric volume of liquid increases slowly with rise of temperature, but at higher temperatures the rate of increase becomes greater. For the purpose of calculation an algebraic expression is usually employed, the number of terms increasing with the range of temperature.

Eliminating the term of molecular fluidity $\Phi$ from the two equations (2) and (3) cited above, we have

$$V^{\frac{2}{3}} = V_k^{\frac{2}{3}} - A\,(T_k - T)^{\frac{1}{5}}. \quad \cdots\cdots (6).$$

where $V$ is molecular volume and $A$ a constant.(1)

Similarly, for specific volume $V_1$:

$$V_1^{\frac{2}{3}} = V_{1k}^{\frac{2}{3}} - A_1\,(T_k - T)^{\frac{1}{5}}. \cdots\cdots (7).$$

TABLE 3.

Chlorobenzene.

| $t$° C | $V^{\frac{2}{3}}$ | | $\varDelta$ | $V$ | | $\varDelta$ |
|---|---|---|---|---|---|---|
| | Obs. | Calc. | | Obs. | Calc. | |
| 0 | 21.51 | 21.49 | − 2 | 99.72 | 99.61 | − 1 |
| 10 | 21.65 | 21.63 | − 2 | 100.7 | 100.7 | 0 |
| 20 | 21.81 | 21.77 | − 4 | 101.7 | 101.6 | − 1 |
| 30 | 21.93 | 21.91 | − 2 | 102.7 | 102.5 | − 2 |
| 40 | 22.07 | 22.06 | − 1 | 103.7 | 103.6 | − 1 |
| 50 | 22.21 | 22.21 | 0 | 104.7 | 104.7 | 0 |
| 60 | 22.37 | 22.36 | − 1 | 105.8 | 105.8 | 0 |
| 70 | 22.52 | 22.52 | 0 | 106.9 | 106.9 | 0 |
| 80 | 22.68 | 22.68 | 0 | 108.0 | 108.0 | 0 |
| 90 | 22.84 | 22.85 | + 1 | 109.1 | 109.2 | + 1 |
| 100 | 23.00 | 23.03 | + 3 | 110.4 | 110.5 | + 1 |
| 110 | 23.18 | 23.21 | + 3 | 111.6 | 111.9 | + 3 |
| 120 | 23.37 | 23.38 | + 1 | 112.9 | 113.2 | + 3 |
| 130 | 23.56 | 23.58 | + 2 | 114.4 | 114.5 | + 1 |
| 140 | 23.74 | 23.77 | + 3 | 115.7 | 115.9 | + 2 |
| 150 | 23.94 | 23.98 | + 4 | 117.1 | 117.4 | + 3 |
| 160 | 24.15 | 24.19 | + 4 | 118.7 | 119.0 | + 3 |
| 170 | 24.36 | 24.42 | + 6 | 120.2 | 120.7 | + 5 |
| 180 | 24.59 | 24.65 | + 6 | 122.0 | 122.4 | + 4 |
| 190 | 24.83 | 24.89 | + 6 | 123.7 | 124.3 | + 6 |
| 200 | 25.08 | 25.15 | + 7 | 125.6 | 126.2 | + 6 |
| 210 | 25.35 | 25.41 | + 6 | 127.7 | 128.0 | + 3 |
| 220 | 25.62 | 25.69 | + 7 | 129.7 | 130.2 | + 5 |
| 230 | 25.93 | 25.98 | + 5 | 132.1 | 132.4 | + 3 |
| 240 | 26.26 | 26.30 | + 4 | 134.7 | 134.9 | + 2 |
| 250 | 26.61 | 26.65 | + 4 | 137.3 | 137.6 | + 3 |
| 260 | 27.01 | 27.01 | 0 | 140.3 | 140.4 | + 1 |
| 270 | 27.42 | 27.40 | − 2 | 143.5 | 143.4 | − 1 |
| 329.2 | 31.29 | 31.01 | −28 | 175.0 | 172.7 | −23 |
| 348.8 | 34.57 | 33.84 | −73 | 203.3 | 196.8 | −65 |
| 358.8 | 40.29 | 39.58 | −71 | 255.7 | 249.1 | −66 |
| 359.2 (critical) | 45.60 | 45.82 | +22 | 307.9 | 310.2 | +23 |

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(1) $A = \frac{C}{K}$ and $A_1 = \frac{C_1}{K_1}$.

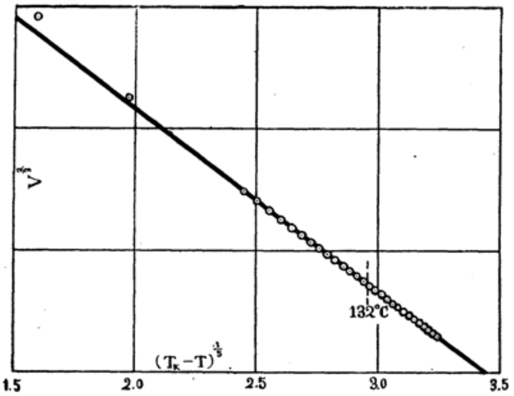

Fig. 4:—Rule (6) for Chlorobenzene.

These relations were found to hold with good accuracy over a wide range of temperature, except near the critical point. As an example, the result for chlorobenzene is given in Fig. 4 and Table 3. For calculation the following numerical equation was used.

$$V^{\frac{2}{3}} = 310.2^{\frac{2}{3}} - 7.50\ (359.2-t)^{\frac{1}{5}}.$$

It will be seen from the above table, that the agreement between observed and calculated values is very good up to near the critical temperature, where a deviation of about 1 to 3 % appears. If suitable correction terms be added, the relation would give a very satisfactory result. This relation suggests the means of calculating the density of liquid and vapour respectively, if it be employed together with the rule of Cailletet and Mathias expressing the sum of two density as a function of temperature.

## Summary.

1. The volume relation of molecular or specific fluidity holds good even when the viscosity changes remarkably with pressure.

2. The volume and temperature relations give results which agree well with each other in all respects.

3. From the two sorts of relations concerning the viscosity, the following equation was obtained,

$$V_k^{\frac{2}{3}} - V^{\frac{2}{3}} = A\,(T_k-T)^{\frac{1}{5}}.$$

which was found to hold with good accuracy.

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

May, 1927.

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