THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART IV.[1]

By Toshizo TITANI.

Received July 22, 1927. Published August 28, 1927.

In part II of this paper we have obtained the following equations expressing the relations between the molecular fluidity Φ defined as $\frac{1}{\eta . V^{\frac{1}{3}}}$ and molecular volume V or temperature T:

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

$$\Phi_K - \Phi = C(T_K - T)^{\frac{1}{3}} \quad \cdots\cdots(2),$$

where K and C are arbitrary constants and Φ_K, T_K critical constants. As regards the specific fluidity Φ_1 referred to one gram, we have obtained exactly the same form of equations, which contain specific volume V_1 and constants K_1, C_1 and Φ_{1K} instead of K, C aud Φ_K. In the present paper some properties of the constants in the above equations will be considered.

First of all the constant B, an effective molecular volume, in equation (1) is of additive nature.[2] In the following table the observed values of B are compared with those calculated by adding respective elementary parts :—

C=6.9, H=5.1, O=7.5, Cl=20.0, F=10.5, double linking=3.0, iso-grouping=0.

TABLE 1. Additivity of constant B.

Substance	Formula	$B_{obs.}$	$B_{calc.}$	Δ
Pentane	C_5H_{12}	95.5	95.7	+0.2%
Isopentane	C_5H_{12}	96.1	95.7	−0.4
Hexane	C_6H_{14}	112.6	112.8	+0.2
Heptane	C_7H_{16}	129.9	129.9	0
Octane	C_8H_{18}	147.9	147.0	−0.6
Methyl-formate	$C_2H_4O_2$	52.0	52.2	+0.4
Ethyl-formate	$C_3H_6O_2$	69.6	69.3	−0.4
Propyl-formate	$C_4H_8O_2$	86.8	86.4	−0.5
Methyl-acetate	$C_3H_6O_2$	68.9	69.3	+0.6
Ethyl-acetate	$C_4H_8O_2$	86.1	86.4	+0.3
Propyl-acetate	$C_5H_{10}O_2$	104.2	103.5	−0.7
Methyl-propionate	$C_4H_8O_2$	85.0	86.4	+1.7
Ethyl-propionate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Methyl-butyrate	$C_2H_{10}O_2$	102.7	103.5	+0.8
Methyl-isobutyrate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Ethyl ether	$C_4H_{10}O$	85.7	86.1	+0.5
Carbon tetrachloride	CCl_4	88.9	86.9	−2.2
Benzene	C_6H_6	82.2	81.0	−1.3
Fluorobenzene	C_6H_5F	85.5	86.4	+1.0
Chlorobenzene	C_6H_5Cl	94.1	95.9	+1.9
Acetic acid	$C_2H_4O_2$	54.0	52.2	−3.3
Carbon dioxide	CO_2	29.5	27.9	−5.4

(1) Part I, this journal, **2** (1927), 95; II, ibid., 161; III, ibid., 196.
(2) It was shown by Batschinski that the constant ω in his formula is also of additive nature. *Z. physik. Chem.*, **84** (1913), 643.

The constants K, C, B and Φ_K in equations (1) and (2) have been reduced by using critical constants from the standpoint of corresponding states. The results are shown in Table 2 and 3.

1). The constant B has a dimension of volume, so that it can be reduced by dividing it with the critical molecular volume V_K :—

$$b_r=\frac{B}{V_K}.$$

2). From the form of equations (1) and (2) it will easilly be seen that the constants K and C can be reduced as follows:

$$k_r=\frac{K.V_K^{\frac{2}{3}}}{\Phi_K},$$

$$c_r=\frac{C.T_K^{\frac{1}{6}}}{\Phi_K},$$

where T_K represents the critical temperature and Φ_K the critical molecular fluidity.

3). The dimension of viscosity η is equal to that of momentum divided by area and from the kinetic theory of gases the velocity v in the momentum may be considered to be proportional to $\sqrt{\frac{T}{M}}$ where T is absolute temperature and M the molecular weight so that :[1]

$$[\eta]=\frac{[\text{Momentum}]}{[\text{Area}]}=\frac{[M][v]}{[V]^{\frac{2}{3}}}=\frac{[M]^{\frac{1}{2}}[T]^{\frac{1}{2}}[R]^{\frac{1}{2}}}{[V]^{\frac{2}{3}}} \quad \cdots\cdots\cdots\cdots(3),$$

where V represents volume and R the gas constant.

Using the above relation, the constants K and C may also be reduced as follows:

$$k_r'=K.M.^{\frac{1}{2}}T_K.^{\frac{1}{2}}V_K^{\frac{1}{3}},$$

$$c_r'=\frac{CM^{\frac{1}{2}}T_K^{\frac{7}{6}}}{V_K^{\frac{1}{3}}}.$$

4). From equations (2) and (3) we obtain the following reduced form of the constant Φ_K,

$$\varphi'_{Kr}=\frac{\Phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}$$

The reduced constants obtained above have actually been calculated for various substances and tabulated below together with the actual constants.

(1) This result has already been pointed out by K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, 2 (1891).

As the values of Φ_K in k_r and c_r, those calculated from equations (1) and (2) have respectively been used.

TABLE 2. Actual constants.

Substance	K	B	C	Φ_K
Pentane	31.8	95.50	251	795.4
Isopentane	32.1	96.10	254	799.5
Hexane	25.4	112.6	219	702.6
Heptane	21.7	129.9	204	660.1
Octane	18.6	147.9	188	612.9
Methyl-formate	43.8	52.04	229	729.5
Ethyl-formate	34.0	69.60	218	696.1
Propyl-formate	27.5	86.82	202	649.3
Methyl-acetate	37.1	68.98	233	742.4
Ethyl-acetate	28.2	86.10	211	674.4
Propyl-acetate	23.8	104.2	196	630.0
Methyl-propionate	28.9	85.04	208	669.2
Ethyl-propionate	23.5	102.9	195	628.5
Methyl-butyrate	23.6	102.7	193	623.5
Methyl-isobutyrate	23.8	102.9	194	624.0
Ethyl ether	33.8	85.69	250	791.0
Carbon tetrachloride	20.4	88.88	147	470.7
Benzene	34.4	82.21	236	756.6
Fluorobenzene	28.8	85.51	200	647.3
Chlorobenzene	24.5	94.12	179	601.1
Acetic acid	(2250)	(0.8997)	(705)	(2291)
Bromine	(4400)	(0.2868)	(688)	(2273)
Carbon dioxide	(3060)	(0.669)	—	—

Note: Numbers in brackets represent quantities referred to one gram.

TABLE 3. Reduced constants.

Substance	k_r	$k'_r \times 10^{-4}$	b_r	c_r	$c'_r \times 10^{-4}$	$\varphi'_{Kr} \times 10^{-4}$
Pentane	1.84	3.98	0.308	1.08	2.34	2.16
Isopentane	1.85	3.95	0.312	1.08	2.34	2.16
Hexane	1.83	3.81	0.306	1.08	2.22	2.05
Heptane	1.83	3.80	0.304	1.09	2.22	2.04
Octane	1.82	3.74	0.302	1.09	2.32	2.12
Methyl-formate	1.82	4.17	0.302	1.08	2.43	2.24
Ethyl-formate	1.82	4.04	0.304	1.09	2.40	2.21
Propyl-formate	1.83	3.94	0.305	1.09	2.35	2.15
Methyl-acetate	1.82	4.39	0.303	1.09	2.57	2.35
Ethyl-acetate	1.82	3.99	0.301	1.09	2.40	2.20
Propyl-acetate	1.82	3.96	0.302	1.10	2.34	2.13
Methyl-propionate	1.82	4.10	0.302	1.09	2.41	2.21
Ethyl-propionate	1.81	3.89	0.299	1.09	2.32	2.12
Methyl-butyrate	1.82	3.92	0.302	1.10	2.33	2.13
Methyl-isobutyrate	1.83	3.90	0.304	1.09	2.30	2.10
Ethyl ether	1.83	4.12	0.304	1.08	2.42	2.24
Carbon tetrachloride	1.88	3.89	0.322	1.11	2.34	2.11
Benzene	1.86	4.58	0.321	1.11	2.76	2.28
Fluorobenzene	1.83	4.32	0.315	1.10	2.54	2.32
Chlorobenzene	1.83	4.41	0.306	1.08	2.57	2.38
Acetic acid	1.86	3.93	0.316	1.10	2.20	1.99
Bromine	1.95	4.29	0.339	1.08	2.67	2.47
Carbon dioxide	1.85	3.67	0.311	—	—	—
Mean	1.84	4.03	0.308	1.09	2.40	2.19

It will be seen from the above table that the respective constant becomes independent of the nature of the substance when it is expressed in reduced value.

Batschinski[1] also calculated the ratio $\frac{\omega}{V_{1K}}$ with various substances, where ω being the limiting volume in the rule proposed by him. This ratio should, according to him, as average be 0.307. Calculating the ratio with liquid carbon dioxide using the data actually measured by P. Phillips[2] near the critical point, it becomes 0.350. In the writer's case, using the same data, the ratio $\frac{B_1}{V_{1K}}$ is 0.311, which is only 1% greater than the average value 0.308.[3]

Reducing the respective quantities and constants in equations (1) and (2) by using the critical constants we have:

$$\frac{\Phi}{\Phi_K}=\frac{KV_K^{\frac{2}{3}}}{\Phi_K}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$1-\frac{\Phi}{\Phi_K}=\frac{CT_K^{\frac{1}{5}}}{\Phi_K}\left(1-\frac{T}{T_K}\right)^{\frac{1}{5}},$$

or for the sake of brevity,

$$\varphi_r=k_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}) \quad \cdots\cdots(4),$$

$$1-\varphi_r=c_r(1-t_r)^{\frac{1}{5}} \cdots\cdots(5),$$

where φ_r, t_r etc. represent reduced quantities or constants.

Using relation (3) stated above, equations (1) and (2) may also be reduced as follows:

$$\frac{\Phi.M.^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=K.M.^{\frac{1}{2}}T_K.^{\frac{1}{2}}V_K^{\frac{1}{3}}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$\frac{\Phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}-\frac{\Phi M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=\frac{CM^{\frac{1}{2}}T_K^{\frac{7}{10}}}{V_K^{\frac{1}{3}}}\left(1-\frac{T}{T_K}\right)^{\frac{1}{5}},$$

or

$$\varphi'_r=k'_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}) \cdots\cdots(6),$$

$$\varphi'_{Kr}-\varphi'_r=c'_r(1-t_r)^{\frac{1}{5}} \cdots\cdots(7),$$

where φ'_r, k'_r etc. represent reduced quantities or constants which are different from φ_r, k_r etc.

---

(1) loc. cit.

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

(3) Cf. paragraph 2 part II of this paper cited above.

It has already been shown that the constants k_r, k'_r, c_r, c'_r, and φ'_{Kr} have universal values independent of the nature of the substance, so that above equations (4), (5), (6) and (7) may be considered to express the theory of corresponding states for molecular or specific fluidity.

Summary.

1. The constant B, the effective molecular volume, is additive.

2. The respective constant in the volume and temperature relations becomes independent of the nature of the substance when it is expressed in reduced form.

3. From the volume and temperature relations of the molecular fluidity the reduced equations of the following form have been obtained.

$$\varphi_r = k_r(v_r^{\frac{4}{3}} - b_r^{\frac{4}{3}}).$$

$$1-\varphi_r = c_r(1-t_r).^{\frac{1}{6}}$$

$$\varphi'_r = k'_r(v_r^{\frac{4}{3}} - b_r^{\frac{4}{3}}).$$

$$\varphi'_{Kr} - \varphi'_r = c'_r(1-t_r).^{\frac{1}{6}}$$

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

July, 1927. The Institute of Physical and Chemical Research, Hongo, Tokyo.