phates in the system $NaPO_3$–$Na_4P_2O_7$ actually exists as a crystalline individual. This is sodium tripolyphosphate, $Na_5P_3O_{10}$, which can be obtained at ordinary temperatures in either one of two crystal forms.

Pittsburgh, Penna. Received September 16, 1940

[Contribution from the Gayley Chemical Laboratory, Lafayette College]

Interrelationships between Fluidity, Volume, Pressure and Temperature in Liquids[1]

By Eugene C. Bingham, Harold E. Adams and Gerald R. McCauslin

Introduction.—A relation between the fluidity and volume of liquids has been proposed by Bachinskii[2] but sufficient data were not then available to give this relation a very critical test, particularly where the change in volume was brought about by varying the pressure instead of the temperature. It is desired in this paper to give the results of a more searching test by the use of more recent data by Bridgman[3] on the relative viscosities and compressibilities of eleven liquids at pressures from one to twelve thousand atmospheres, at the two temperatures 30 and 75°.

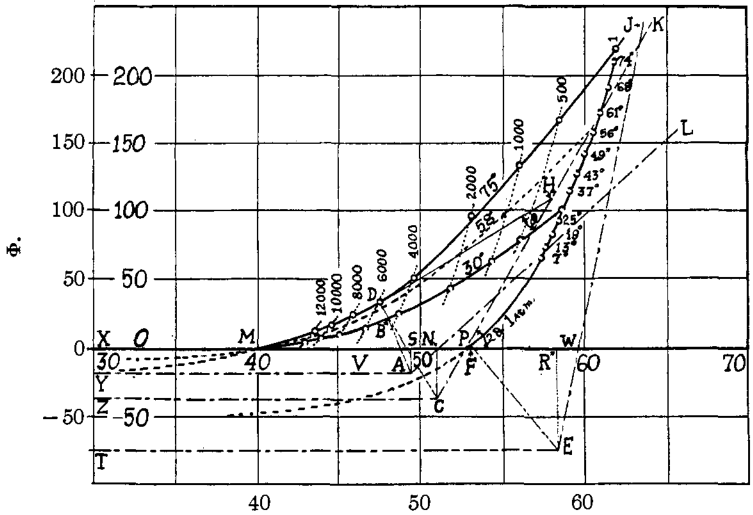

Fig. 1.—Φ *vs.* *V* isotherms of ethyl alcohol at 30 and 75° and isobar at 1 atmosphere.

Neither Bridgman himself nor other worker has found a formula to fit his data. Moreover, Bingham and Coombs,[4] in studying new fluidity temperature data for compounds of high molecular weight, have discovered that in a given homologous series, as the molecular weight increases, the fluidity–volume curves deviate more and more from the linear Bachinskii formula

$$V - \Omega = A\varphi \qquad (1)$$

and pass into a hyperbolic form, which may be written, at least as a first approximation, as

$$V - \Omega = A\varphi - B/\varphi \qquad (2)$$

Bachinskii called Ω the molar limiting volume, $V - \Omega$ the molar free volume which we designate by F_B, and A and B are constants. In comparing the constants of the isobars, where the temperature alone is varied, with those of the isotherms, where the pressure is alone varied, it becomes desirable to distinguish them by subscripts of pressure or temperature as $[A]_P$ and $[A]_T$, etc. Bingham and Coombs found eq. (2) to be sufficiently satisfactory for studying changes in volume and fluidity brought about by varying the temperature and the chemical composition, but it was nevertheless noted that the fit is less perfect when the volume is very small. Time did not permit the elimination of the discrepancy.

As a step in the solution, Bingham, R. G. Volkman[5] and J. L. Petrokubi, working in this Laboratory, found that even a substance which is regarded as obeying the Bachinskii formula particularly well, such as pentane, will, upon severe cooling, reach values of fluidity and volume where the use of the hyperbolic equation is desirable.

Procedure.—The fluidities and molecular volumes were calculated from the original relative values and plotted. A plot of the two isotherms

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(1) Original manuscript received August 15, 1939.

(2) Bachinskii, *Z. physik. Chem.*, **82**, 86 (1931).

(3) Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1931); **61**, 57 (1926); **62**, 187 (1927).

(4) Coombs, Thesis, Lafayette College, 1935, not yet published.

(5) Volkman and Petrokubi, Theses, Lafayette College, 1936, unpublished. The atomic constants most used, for calculating $[\Omega]_P$ as modified from Bachinskii's values by A. E. Holderith and C. E. Grant, using new and more extensive data are CH_2 = 17.76, O = 9.65, H = 4.46, S = 15.63, Cl = 18.79, Br = 21.35, I = 31.74, N = 3.17.

at 30 and 75° (Table I) is given in Fig 1 and the corresponding isobar at a pressure of one atmosphere is added, using the data of Thorpe and Rodger in Table II. From the points on the curves on which the pressures and temperatures are noted approximately, it is observed that an indefinite number of other isotherms and isobars could be obtained, thus forming a network as indicated by dotted curves. All of the curves seem to be hyperbolic and they definitely cross the volume-axis at positive values. The isothermals both cross the axis close to 39.7 cc. independent of the temperature, but at pressures of 17,200 atmospheres at 30° and 22,900 atmospheres at 75°, the isobar of one atmosphere crosses at 53.0 cc., which corresponds to a temperature below the melting point of 161°K.

TABLE I

A COMPARISON OF THE FLUIDITIES AND VOLUMES OF ETHYL ALCOHOL AT 30 AND 75° BUT UNDER VARYING PRESSURES, AFTER BRIDGMAN[2]

P, kg./sq. cm.	φ obsd.	V obsd.	V calcd.	% Dev.
		30°C.		
1	100.7	58.72	58.59	0.22
500	77.64	56.09	56.09	.00
1,000	62.68	54.28	54.36	.15
2,000	43.06	51.80	51.80	.00
4,000	24.00	48.67	48.66	.10
6,000	14.73	46.56	46.56	.00
8,000	9.420	45.05	44.99	.13
10,000	6.112	43.78	43.78	.00
12,000	4.047	42.71	42.90	.44
			Av. %	.106
		75°C.		
1	218.8	61.82	61.30	.82
500	167.9	58.40	58.40	.00
1,000	133.1	56.19	56.25	.11
2,000	89.58	53.18	53.18	.00
4,000	51.06	49.68	49.65	.06
6,000	33.43	47.42	47.42	.00
8,000	23.08	45.76	45.74	.04
10,000	16.56	44.45	44.45	.00
12,000	11.97	43.43	43.408	.05
			Av. %	.12

TABLE II

A COMPARISON OF THE FLUIDITIES AND VOLUMES OF ETHYL ALCOHOL AT VARIOUS TEMPERATURES AND AT 1 ATMOSPHERE OF PRESSURE, AFTER THORPE AND RODGER[6]

$T°$	φ	V obsd.	V calcd.	% error
7.16	65.2	57.311	57.320	0.02
13.23	73.7	57.680	57.684	.01
19.22	82.7	58.048	58.048	.00
25.24	92.7	58.426	58.426	.00
31.89	104.6	58.854	58.850	.01
37.51	115.7	59.222	59.222	.00
42.84	127.0	59.586	59.584	.003
49.37	141.9	60.037	60.039	.003
55.57	157.4	60.489	60.489	.00
61.07	172.0	60.898	60.895	.004
67.55	190.4	61.400	61.389	.02
73.57	209.6	61.884	61.884	.00
			Av. %	.006

It is now obvious that the approximation of Bingham and Coombs is not sufficiently close, since, according to eq. (2), the fluidity can reach a zero value only when the volume has a very large *negative* value. This difficulty is fortunately very easily removed by adding one more constant D so that the fluidity–volume equation becomes

$$V - \Omega = A(\varphi + D) - B/(\varphi + D) \tag{3}$$

or somewhat more simply

$$V - C = A\varphi - B/(\varphi + D)$$

where

$$C = \Omega + AD$$

The equation of one asymptote is $\varphi = -D$ and the lines YA, ZC and TE are examples, the equation of the other asymptote is $V - C = A\varphi$ and the lines AL, CK and EJ are examples; the points A, C and E are the vertices, and the lines AB, CD and EF represent the minor semi-axes of the hyperbolas. A line tangent to the curve at 75° at the point D intersects the asymptote CK at H, and the angle between the line DH and the asymptote is ϑ. The distance DH is the semi-major axis $b/2$ and the length CD $= a/2$, hence $\tan \vartheta = a/b$. The angle ϑ is the angle of rotation necessary to put the hyperbola into the standard form, Ω is the distance from the φ-axis to the vertex in horizontal translation and the constant D is similarly the amount of vertical translation. The angle made by the asymptote in crossing the volume-axis, *e. g.*, KPW, is equal to 2ϑ, and $\cot 2\vartheta = A$ of eq. (3). The equation for this asymptote tells us that the point of intersection, *e. g.*, P, is distant from the fluidity-axis by $V = C$, since φ then is zero. Similarly the curves cross the volume-axis at a point obtained by making $\varphi = 0$ in eq. (3), *i. e.*

$$V_0 = \Omega + AD - B/D \tag{4}$$

where V_0 is the volume corresponding to the point of intersection of the curve with the volume-axis, AD is for the temperature curve at 30° the small distance SN; it is obviously $D \cot 2\vartheta$. The ratio B/D for this curve now turns out to be

$$B/D = \Omega + AD - V_0 \tag{4a}$$

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[6] Thorpe and Rodger, *Phil. Trans. Roy. Soc.* (London), **185A**, 397 (1894).

which is the intercept of the asymptote on the volume-axis less the intercept of the corresponding curve on the same axis and this is for the 30° curve the distance MN.

Calculation of Constants.—The constants of the equation were calculated by selecting four points. They are given in Tables III and IV. Let

$$\frac{V_4 - V_3}{\varphi_4 - \varphi_3} - \frac{V_3 - V_2}{\varphi_3 - \varphi_2} = \alpha \qquad (5)$$

and

$$\frac{V_3 - V_2}{\varphi_3 - \varphi_2} - \frac{V_2 - V_1}{\varphi_2 - \varphi_1} = \beta \qquad (6)$$

and

$$\alpha + \beta = \gamma \qquad (7)$$

then

$$D = \frac{\alpha\varphi_3\varphi_4 + \beta\varphi_1\varphi_2 - \gamma\varphi_1\varphi_4}{\alpha(\varphi_1 - \varphi_3) - \beta(\varphi_2 - \varphi_4)} \qquad (8)$$

$$B = \frac{\alpha(\varphi_3 + D)(\varphi_2 + D)(\varphi_4 + D)}{\varphi_2 - \varphi_4} \qquad (9)$$

$$A = \frac{V_2 - V_1}{\varphi_2 - \varphi_1} - \frac{B}{(\varphi_2 + D)(\varphi_1 + D)} \qquad (10)$$

TABLE III

THE CONSTANTS AND PERCENTAGE DEVIATION BETWEEN OBSERVED AND CALCULATED VOLUMES FROM DATA OBTAINED AT ONE ATMOSPHERE BY VARIATION OF THE TEMPERATURE

Compound	$A_{1\text{ atm.}}$	$B_{1\text{ atm.}}$	$C_{1\text{ atm.}}$	$D_{1\text{ atm.}}$	V_{m_0} 1 atm.	% Dev.
[a]Methyl alcohol	0.02260	−69.190	37.180	−323.41	44.489	0.033
Ethyl alcohol	.019322	491.70	59.559	75.47	58.101	.005
Propyl alcohol	.014201	1831.74	83.436	152.02	81.277	.011
Butyl alcohol	.03088	588.82	96.471	60.022	94.618	.145
Heptyl alcohol	.07860	172.08	144.59	18.487	143.14	.14
Octyl alcohol	.09100	168.04	162.85	16.112	161.38	.03
Hexadecyl alcohol	.09624	509.35	315.11	17.351	313.44	.0
[a]Ethyl ether	.045063	−60.656	85.165	−539.87	109.493	.0
Ethyl bromide	.033085	643.43	69.90	17.818	69.31	.0
[a]Ethyl iodide	.055018	−649.91	71.87	−1104.87	150.86	.0
					Av. %	.036

[a] For these compounds the points were so nearly on a straight line, *cf.* Table XIII, that the effort to find the constants of the hyperbola were not significant.

TABLE IV

THE CONSTANTS AND PERCENTAGE DEVIATIONS FOR COMPOUNDS BETWEEN OBSERVED AND CALCULATED VOLUMES FROM DATA OBTAINED FROM ISOTHERMS AT 30 AND 75°

Compound	Temp., °C.	A_T	B_T	C_T	D_T	Av. % error
Methyl alcohol	30	0.039497	613.69	35.647	74.407	0.07
	75	.029817	2233.5	37.536	223.00	.27
Ethyl alcohol	30	.09140	195.91	51.021	19.007	.11
	75	.04753	503.51	52.863	38.161	.12
Propyl alcohol	30	.18396	46.242	66.027	4.8294	.09
	75	.09949	162.09	66.840	15.262	.14
i-Butyl alcohol	30	.27320	28.4965	83.377	2.0707	.25
	75	.12880	98.365	82.850	7.3624	.35
i-Amyl alcohol	30	.46910	13.004	96.836	0.98864	.52
	75	.14910	88.831	99.146	5.684	.30
Ethyl ether	30	.024470	2505.2	97.300	93.437	.47
	75	.033274	2923.9	94.160	118.63	.25
Ethyl bromide	30	.045459	553.11	65.200	42.677	.63
	75	.019441	4367.7	80.150	159.94	.24
Ethyl iodide	30	.066290	374.82	70.675	29.878	.10
	75	.053350	954.60	73.970	58.875	.08
Acetone	30	.035010	195.99	65.835	81.607	.22
	75	.058077	270.38	57.488	25.098	.07
Carbon bisulfide	30	.001644	1187.9	79.187	331.12	.23
	75	.022514	6798.2	65.330	366.03	.19
Carbon dioxide[a]	30	.015709	−13.136	34.999	−1624.1	.35
	32	.020365	−70.424	28.35	−31338.2	.27
	35	.021217	−810.80	28.262	−2373.1	.11
					Av.	.234

[a] Phillips, *Proc. Roy. Soc.* (London), **87A**, 48 (1912).

and

$$C = \frac{B}{\varphi + D} - A\varphi + V \qquad (11)$$

The use of the supplementary equations (5), (6) and (7) was suggested to us privately by Dr. G. Raymond Hood of Miami University.

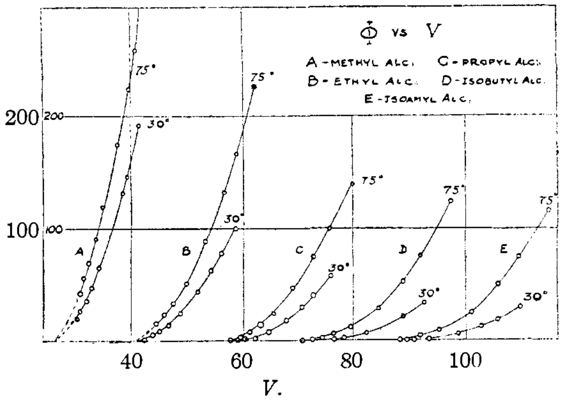

Fig. 2.

The higher alcohols give fluidity–volume curves which differ from those of ethyl alcohol in that for a given fluidity the molecular volumes increase steadily with the molecular weight and the curves meet the volume-axis at a smaller and smaller slope. These are shown for 30 and 75° in Fig. 2.

TABLE V

THE RELATION BETWEEN FLUIDITY AND VOLUME FOR MERCURY AT 1 ATMOSPHERE BUT AT VARIOUS TEMPERATURES, USING THE EQUATION $V = 0.013218\varphi + 13.959$

T	φ	V	V calcd.	% Dev.
273	59.4	14.756	14.744	0.10
283	62.1	14.782	14.780	.01
293	64.3	14.809	14.809	.00
303	66.8	14.836	14.842	.04
313	68.6	14.863	14.866	.02
323	71.0	14.888	14.898	.10
333	72.9	14.917	14.923	.04
343	74.9	14.944	14.949	.03
353	76.7	14.971	14.973	.02
363	78.1	14.998	14.991	.04
373	80.0	15.025	15.015	.08
			Av.	.048

TABLE VI

THE VOLUMES AND FLUIDITIES OF MERCURY AT 75°C. AT VARIOUS PRESSURES, DEMONSTRATING THE VALIDITY OF THE EQUATION $V = 0.036668\varphi + 12.2167$

V obsd.	P obsd.	φ obsd.	V calcd.	% Dev.
14.976	1	74.627	14.953	−0.12
14.827	2,000	71.429	14.836	+ .06
14.712	4,000	68.353	14.733	+ .12
14.607	6,000	65.445	14.616	+ .06
14.511	8,000	62.578	14.511	.00
14.426	10,000	59.737	14.407	− .10
			Av.	.07

In order to be able to consider the simplest sort of substance first in a logical procedure, the fluidity–volume curves for mercury will now be included, since that is a monatomic liquid. The data are listed in Tables V and VI, the curves being shown in Fig. 3.

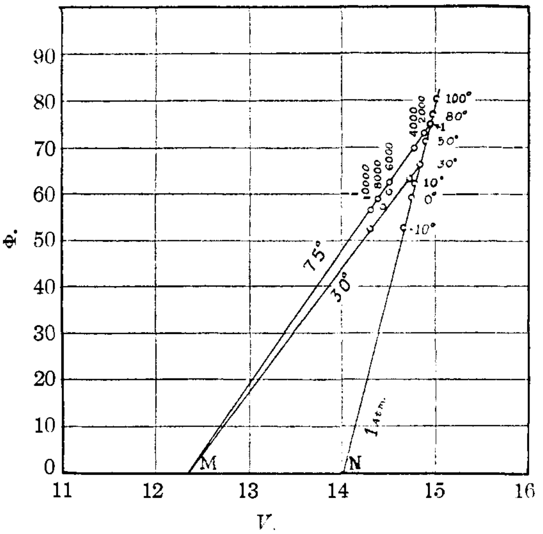

Fig. 3.—Φ *vs.* V isotherms of mercury at 30 and 75° and isobar of mercury at 1 atmosphere.

Discussion.—Both the isothermal and the isobaric curves of mercury are nearly linear but they are not coincident. For the equation of the isobar at one atmosphere by the method of least squares is

$$V = [A]_P\varphi + [C]_P \qquad (12)$$

where $[A]_P = 0.013218$ and $[C]_P = 13.959$. The mean deviation between the observed and calculated values is 0.05%. The isothermal is not very well determined by the small number of observed points available. At 75° we have the equation of the isotherm

$$V = [A]_T\varphi + [C]_T \qquad (13)$$

where $[A]_T = 0.3668$ and $[C]_T = 12.2167$. The mean deviation is less than 0.1 per cent.

The significant thing about the φ *vs.* V curves for mercury is that, at atmospheric pressure, on lowering the temperature the fluidity decreases to a zero value as the volume decreases and the volume is some 1.7 ml. *greater* than would have been the case had the fluidity been reduced to zero by means of pressure alone. In other words, if the entire family of isothermals were available, there would be one starting at N with a fluidity of zero and—assuming that all of the isothermals pass through the point M—extending to M, and of course with no appreciable decrease in fluidity. The problem then is to explain how the fluidity decreases rapidly to zero by lowering the temperature after which a further decrease in volume may be made without effect on the fluidity.

If we follow the principle of seeking the simplest explanation, we must adhere to the law that *the fluidity is directly proportional to the free volume.* Then the largest volume that the liquid can have with a fluidity of zero must correspond to its limiting volume at the lowest possible pressure, assumed to be the vapor pressure of the liquid, because at that volume the molecules must touch each other in some form of close packing. If then the molecules are elastic, and permit themselves to occupy a smaller and smaller volume under increased pressure while the molecules are continually in contact, it would be feasible to explain compression without loss of fluidity. According to this view, at any fluidity, the difference between the isothermal and the isobar at the lowest possible pressure represents the molecular compression V_a, or in this case we might appropriately speak of the atomic compression.

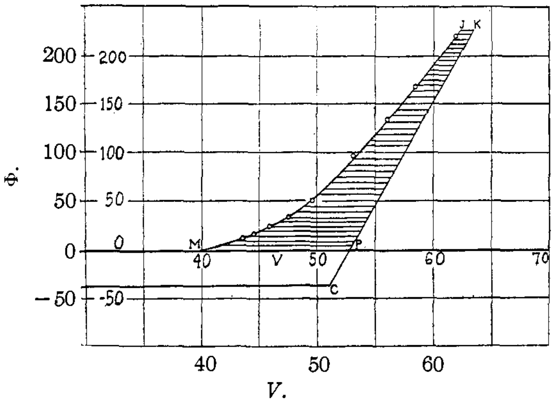

Fig. 4.—The molecular compression of ethyl alcohol at various fluidities.

When our consideration comes to the more complex polyatomic molecules this molecular compression V_m becomes many times as great as that shown by mercury, increasing steadily with the complexity. There is also another degree of complexity which must now be referred to. As has already been stated, the fluidity–volume curves whether isobars or isothermals are hyperbolic. If again we adhere to the law that the fluidity is directly proportional to the free volume, it appears that some theory is required to explain why the simple expression of this law in the equation

$$V - \Omega = A\varphi \qquad (14)$$

which does apply to simple liquids, *e. g.*, mercury, does not hold, Fig. 4. At high fluidities all liquids follow approximately this fluidity law but at low fluidities the more complex ones all depart from it more and more as the fluidity is reduced. This effect is assigned to the internal pressure, for when one plots the isobar for one atmosphere, the result is not a simple lowering of the temperature but also a steadily increasing internal pressure, which will also tend to decrease the volume; if that decrease in volume took place between the *atoms* of the molecule, it would not cause a lowering of the fluidity because in the process of shearing a liquid, the molecular arrangement remains intact.

If therefore this molecular compression is denoted by V_m, we find it to be the difference between the theoretical volume calculated by eq. (1) and the observed volume as given by eq. (3), thus

$$V_m = B/(\varphi + D) \qquad (15)$$

or

$$\varphi = B/V_m - D$$

and when $\varphi = 0$

$$D = B/V_{m_0}$$

so the molar compression volume at zero fluidity is

$$V_{m_0} = B/D \qquad (16)$$

which indicates that the constants B and D are closely related. To bring this out more clearly, there are given the values for this ratio for a number of alcohols of differing complexity in Table VII. From the volume of B/D in the above table we have derived two formulas for calculating the values of B/D. They are $[B/D]_{30°} = 1.33\,n + 7.02$ and $[B/D]_{75°} = 1.14\,n + 9.14$ where n is the number of methylene groups in the molecule. They show mean deviations of a little over 5%.

Table VII

The Relation between the Constants B and D for Some Alcohols

Alcohol	T_C°	B	D	$B/D = V_{m_0}$ obsd.
Methyl	30	613.69	74.407	8.2477
	75	2233.5	223.00	10.015
Ethyl	30	195.91	19.007	10.307
	75	503.51	38.161	13.195
Propyl	30	46.242	4.8294	9.57
	75	162.09	15.262	10.621
Isobutyl	30	28.497	2.0707	13.778
	75	98.365	7.3624	13.360
Isoamyl	30	13.004	0.98864	13.153
	75	88.831	5.684	15.628

It is now possible to express the fluidity as

$$\varphi = B/(1/V_m - 1/V_{m_0}) \qquad (17)$$

The curves for the isotherms of 30 and 75° in Fig. 5 were obtained by plotting the observed values of the fluidity against $1/V_m - 1/V_{m_0}$ obtained from the observed molecular volumes. The curves are linear and pass through the origin. The curves for the isobars of the same alcohols are given in Fig. 6. The data for the curves are given in Tables VIII, IX and X.

This is the most fitting place to refer to the extraordinary fact that the fluidity–volume curve of mercury unlike that of most other liquids shows a small but distinct and possibly significant negative curvature, at temperatures well below the boiling point. All liquids might show this behavior near the critical temperature. There are several of the more simple organic liquids which give negative values for B and D of eq. (3) and therefore as the volume increases the fluidity approaches an upper limit. In every one of these cases the observed fluidities plotted against the volumes are very nearly linear and a very slight observational error might determine whether D was to be given the plus or minus sign. We have therefore preferred in these cases simply to employ the linear equation (14) for which the constants are given in Table XI.

TABLE VIII

THE ISOTHERMAL OF ETHYL ALCOHOL AT 30°

$A = 0.09140$; $B = 195.91$; $C = 51.021$; $D = 19.007$

P kg./sq. cm.	φ	V Eq. (1)	V obsd.	V_m	$1/V_m \times 10^{-1}$	$(1/V - 1/V_{m_0}) \times 10^{-1}$
1	100.7	60.225	58.72	1.505	6.6445	5.6743
500	77.64	58.117	56.09	2.027	4.9334	3.9632
1000	62.68	56.750	54.28	2.470	4.0486	3.0784
2000	43.06	54.957	51.80	3.157	3.1676	2.1974
4000	24.00	53.214	48.67	4.544	2.2007	1.2305
6000	14.73	52.367	46.56	5.707	1.5722	0.6020
8000	9.420	51.882	45.05	6.832	1.4637	0.4935
10000	6.112	51.580	43.78	7.800	1.2821	0.3119
12000	4.047	51.391	42.71	8.681	1.1519	0.1817
....	0	....	...	10.307	0.9702	0

TABLE IX

THE ISOTHERMAL OF ETHYL ALCOHOL AT 75°

$A = 0.04753$; $B = 503.51$; $C = 52.863$; $D = 38.161$

P kg./sq. cm.	φ	V Eq. (1)	V obsd.	V_m	$1/V_m \times 10^{-1}$	$(1/V_m - 1/V_{m_0}) \times 10^{-1}$
1	218.8	63.262	61.82	1.442	6.9348	6.1769
500	167.9	60.843	58.40	2.443	4.0933	3.3354
1000	133.1	59.189	56.19	2.999	3.3344	2.5765
2000	89.58	57.121	53.18	3.941	2.5374	1.7795
4000	51.06	55.290	49.68	5.510	1.8149	1.0570
6000	33.43	54.452	47.42	7.032	1.4221	0.6642
8000	23.08	53.960	45.76	8.200	1.2195	.4616
10000	16.56	53.650	44.45	9.200	1.0870	.3291
12000	11.97	53.432	43.43	10.002	0.9998	.2419
....	0	52.263	...	13.194	0.7579	0

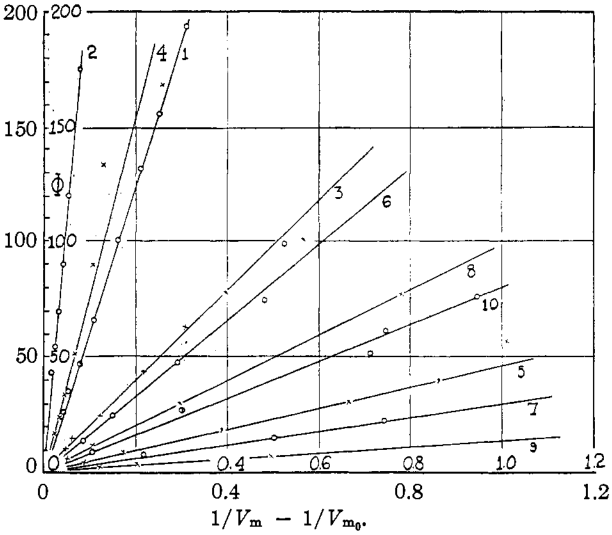

Fig. 5.—Curves of the fluidity of various alcohols plotted against $1/V_m - 1/V_{m_0}$ with the temperature kept constant at 30 or 75°: 1, methyl, 30°; 2, methyl, 75°; 3, ethyl, 30°; 4, ethyl, 75°; 5, propyl, 30°; 6, propyl, 75°; 7, isobutyl, 30°; 8, isobutyl, 75°; 9, isoamyl, 30°; 10, isoamyl, 75°.

TABLE X

THE ISOBAR OF ETHYL ALCOHOL AT 1 ATM.

$A = 0.019322$; $B = 491.70$; $C = 59.559$; $D = 75.47$

T	φ	V Eq. (1)	V obsd.	V_m	P $(1/V_m \times 10^{-1}$	$(1/V_m - 1/V_{m_0}) \times 10^{-1}$
7.16	65.2	60.819	57.311	3.508	2.8506	1.3157
13.23	73.7	60.983	57.680	3.303	3.0276	1.4927
19.22	82.7	61.157	58.048	3.109	3.2165	1.6816
25.24	92.7	61.350	58.426	2.924	3.4199	1.8850
31.89	104.6	61.580	58.854	2.726	3.6684	2.1335
37.52	115.7	61.795	59.222	2.573	3.8865	2.3516
42.84	127.0	62.013	59.586	2.427	4.1203	2.5854
49.37	141.9	62.301	60.037	2.264	4.4169	2.8820
55.57	157.4	62.600	60.489	2.111	4.7371	3.2022
61.07	172.0	62.882	60.898	1.984	5.0403	3.4954
67.55	190.4	63.238	61.400	1.838	5.4407	3.9058
73.57	209.6	63.609	61.884	1.725	5.7971	4.2622
....	0	....	....	6.5152	1.5349	0

TABLE XI

CONSTANTS FOR EQUATION $V = A\varphi + C$, WHICH IS SUFFICIENTLY EXACT TO REPLACE EQUATION (3) IN THE CASES OF THE FOLLOWING COMPOUNDS

Compound	A	C	Av. % dev.
Isobar of methyl alcohol	0.018346	37.361	0.063
Isobar of diethyl ether	.040621	86.445	.25
Isobar of ethyl iodide	.054252	71.3005	.004
Isobar of mercury	.013218	13.959	.048
Isotherm of mercury	.036039	12.257	.054

Referring back to Fig. 1 for ethyl alcohol, it now appears that at one atmosphere of pressure, we would expect the limiting volume by the fluid-

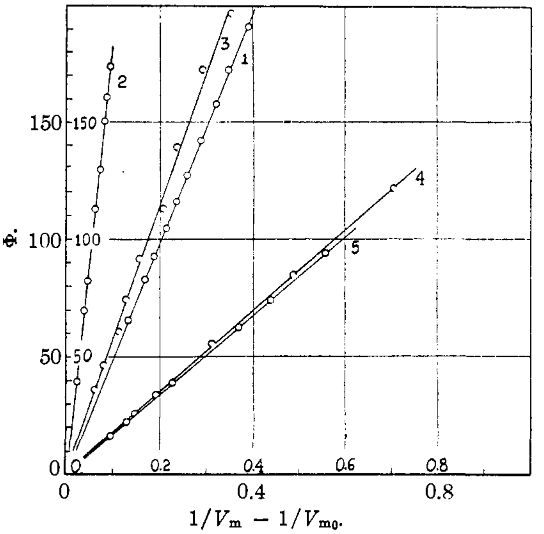

Fig. 6.—Curves of the fluidity of various alcohols plotted against $1/V_m - 1/V_{m_0}$ with the pressure of one atmosphere: 1, ethyl; 2, propyl; 3, butyl; 4, heptyl; 5, octyl.

ity law to be the distance from the φ-axis to the point W but the actual limiting volume is taken to P only, due to the effect of the internal pressure; and external pressure can certainly bring about a further compression to the point M, the fluidity for any volume greater than 40 cc., depending upon the temperature. By making the correction for the compression of the molecules it appears possible to reduce the more complex pattern of the ethyl alcohol type to the simpler mercury type.

It was stated that the values of V_0 for ethyl alcohol at 30 and 75° appear to be identical. The extrapolation of these curves is fraught with uncertainty. The identity of the values may unconsciously be the result of "wishful thinking," although the authors had no idea that the values of V_0 "should be" identical at any particular positive value. We were clear only that the value should not be minus infinity, which our simple hypothesis demanded.

Even if the present hypothesis does, in some way not yet understood, require all of the isothermals to have the same volume at zero fluidity, that does not prove the validity of the hypothesis or its consequences deduced in this paper. That validity rests upon the faithfulness with which our formula reproduces the observed data. They are limited in their range and when, if ever, that range is extended this hypothesis will be given a severer test. This paper is presented to exhibit certain consequences which may be deduced if this hypothesis is correct. If, however, another hypothesis requires a different formula, *e. g.*, an exponential formula, then it should not only fit the data over a wider range but the characteristics of the behavior of fluids under varying conditions should be predictable in various ways which would no doubt contradict the predictions which follow from our hypothesis.

The importance of the values of V_0 is considerable. In the following Table XII, the values of V_0 have been calculated from the precise constants given in Table IV. This table shows that for all of the substances for which we have data, the values of the molar volume at zero fluidity are independent of the temperature. The average deviation is 1%. This signifies that the identity is not peculiar to ethyl alcohol or any other one substance. It is a characteristic of all for which data are available, whether the substances are associated or not.

TABLE XII

MOLAR VOLUMES OF VARIOUS COMPOUNDS AT ZERO FLUIDITY FOR 30 AND 75° ISOTHERMALS

Substance	30°	75°	
	V_0 obsd.	V_0 obsd.	V_0 calcd.
Methyl alcohol	27.4	27.5	27.1
Ethyl alcohol	40.7	39.7	41.3
Propyl alcohol	56.4	56.2	55.6
i-Butyl alcohol	69.6	69.5	69.8
i-Amyl alcohol	83.7	83.5	84.0
Ethyl ether	70.5	69.5	69.8
Water	12.3		12.8
Ethyl bromide	52.2	52.8	52.5
Ethyl iodide	58.1	57.8	58.0
Acetone	41.8	46.7	44.3
Carbon disulfide	43.3	43.1	43.2

The equation used in calculating V_0 is

$$V_0 = C - B/D$$

and V_0 shares the same precision that the constants C, B and D have, *i. e.*, V_0 would have the doubtful quality of an extrapolated curve if we think of it as a real point to be obtained experimentally. If, on the other hand, we think of it as a constant, of significance in explaining the data we have at hand over *a limited range*, its precision has meaning. It is somewhat like the data on the contraction of gases with the temperature, which indicate the ideal absolute zero of temperature and not the boiling point or freezing point.

The approximate identity of V_0 at the two temperatures was first noted upon plotting the fluidity–volume curves, but the constants A, B, C and D were calculated without reference to that seeming fact, and the values of V_0 are calculated only now in preparing the paper for publication. The average deviation from the mean is only 1% which is a surprisingly low value. It is often possible to test a theory by means of apparently unconnected knowledge. For example, it has been reported that molecular volumes are additive, and therefore the volumes at zero fluidity should exhibit this characteristic. We have only the one homologous series of alcohols and they are usually regarded as associated and two of them are not *normal*. It turns out, however, that the volume increases linearly with the molecular weight according to the equation

$$V_0 = 14.24\,n + 12.85$$

where n is the number of methylene groups in the molecule (Table XII). The average deviation from the mean is again 1%. The equation applies not only to isobutyl alcohol but also to the metameric substance diethyl ether. This equation signifies that each methylene group increases the molar volume for water by 12.85 cc. The value obtained from the experimental data for water is 12.311.

With the scant data available we are able to assign values to several of the atomic constants, which have a certain interest. They are: oxygen, 1.55; carbon, 2.94; hydrogen, 5.65; bromine, 18.41; iodine, 23.82; and sulfur, 20.13. The values are all positive; they do not follow the order of atomic weights but seem to fit in with our knowledge of atomic volumes of the elements.

Whether this minimal volume of a liquid is truly the lowest volume that the liquid can have in the undercooled condition without changing its identity as by shearing of the electrons from the atoms is for us at present merely a subject for speculation.

Reverting now to the data for mercury, there are an infinite number of isothermals and isobars with their appropriate "constants." In considering gases, it is customary to employ the gas laws and compare gases under the conventionally agreed upon "standard conditions." With laws analogous to those of Boyle and Charles it would be possible in the case of liquids also to avoid complexity by comparing all liquids at the standard conditions of one atmosphere of pressure and 0°.

When dealing with liquids, the volume which is subject to expansion and contraction is the free volume F, and the pressure, Π, is not the impressed pressure P but rather this plus the internal pressure, so there naturally suggest themselves the two laws

$$F\Pi = [K]_T \qquad (18)$$

and

$$F = [K]_P T \qquad (19)$$

which may be combined to give

$$F\Pi = R_L T \qquad (20)$$

In Table XIII for mercury the equation (18) in the form

$$F(P + 39{,}780) = 103{,}410 \qquad (21)$$

has been obtained by the method of least squares. The deviation between the observed and calculated values shows a mean value of 0.11%. In Table XIV the equation (19) in the form $F = 2.697 \times 10^{-3}\,T$ is tested for $P = 1$ atm. The mean deviation is 0.12% where T is the absolute temperature. The method of least squares and t would lead to a number other than 273 customarily used in converting centigrade to absolute. The value obtained was 272.8° so the direct proportionality of equation (19) was assumed. The mean deviation between the observed and calculated values is 0.12%. It is of interest to note that the free volume of mercury under standard conditions of 1 atm. and 0° is 0.736 ml. instead

TABLE XIII

THE FREE VOLUMES AND PRESSURES OF MERCURY AT 75° AT VARIOUS PRESSURES, DEMONSTRATING THE VALIDITY OF THE EQUATION

$1/F = 9.6702 \times 10^{-6}\,(P + 39{,}780)$..............(21)

V obsd.	P obsd.	$1/F$ obsd.	$1/F$ calcd.	% Dev.
14.956	1	0.38373	0.3847	+0.26
14.827	2,000	.40371	.4040	+ .07
14.712	4,000	.42337	.4234	+ .02
14.607	6,000	.44306	.4426	− .09
14.511	8,000	.46275	.4619	− .18
14.426	10,000	.48169	.4818	+ .04
			Av.	.11

TABLE XIV

THE FREE VOLUMES, F, AND ABSOLUTE TEMPERATURES OF LIQUID MERCURY AFTER BINGHAM AND THOMPSON[7]

$\Omega_{1\text{ atm.}} = 14.019;\ F = 2.697 \times 10^{-3}\,T$

T, obsd.	V, obsd.	F, obsd.	F, calcd.	% Dev.
273	14.756	0.7369	0.7362	−0.1
283	14.782	.7629	.7632	.0
293	14.809	.7899	.7901	+ .1
303	14.836	.8159	.8171	.1
313	14.863	.8539	.8441	−1.1
323	14.888	.8689	.8710	+0.1
333	14.917	.8979	.8980	.0
343	14.944	.9249	.9249	.0
353	14.971	.9519	.9519	.0
363	14.998	.9789	.9788	.0
373	15.025	1.0059	1.0058	.0

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(7) Bingham and Thompson, THIS JOURNAL, **50**, 2878 (1928).

of 22.4 liters. The value of R_L is 0.107 liter atmospheres.

Conclusions

1. The fluidity–volume curves of the aliphatic alcohols follow the hyperbolic equation of the form

$$V = A\varphi - B/(\varphi + D) + C$$

whether the change in volume is due to the variation of temperature or pressure. It also becomes the earlier Bachinskii equation when $\varphi + D$ is large in respect to B.

2. To lower the fluidity a given amount requires a quite different reduction in the volume depending upon whether it is brought about by pressure or by cooling. This curious and very important difference may be explained as the result of the high elasticity of the atoms and molecules. According to this view, at the lowest practicable pressure, *i. e.*, the vapor pressure of the liquid, the constant $[C]_P$ represents the volume of the molecules in one mole in the loosest form of close packing, at which the fluidity must be zero. On compression, with the fluidity remaining at zero, the molar volume is gradually reduced to its minimal value of $[C]_T$.

3. The minimal molar volume for zero fluidity is independent of the temperature of the liquid, of course in the undercooled state. Whereas this minimal volume, V_0, like the absolute zero of temperature, may seem remote or even somewhat hypothetical, nevertheless its value is obtained from reliable data as a constant which can be made precise. From the limited data available, it appears that this minimal volume may be calculated from atomic constants, *e. g.*, O = 1.55; C = 2.94; H = 5.65; Br = 18.41; I = 23.82; and S = 20.13.

4. When the monatomic liquid, mercury, is heated, the volume varies as a linear function of the temperature centigrade, t. This becomes a direct proportionality when 272.8° is added to the temperature.

5. The fluidity of mercury varies linearly with the molar volume either $[V]_P$ or $[V]_T$ If there is subtracted from either of these volumes the corresponding values for the limiting volume, there will be obtained the free volumes for isobar $[F]_P$ and isotherm $[F]_T$. The fluidities $[\varphi]_P$ and $[\varphi]_T$ are directly proportional to these free volumes.

6. When mercury is subjected to pressure, the rheolar concentration, *i. e.*, the reciprocal of the molar free volume, is a linear function of the pressure. If 39,780 is added to the pressure in atmospheres, the rheolar concentration is directly proportional to the total pressure. This correction to the applied pressure of 39,780 atmospheres, is a measure of the internal pressure. For this quantity, Prof. T. W. Richards[8] obtained the value of 41,300.

7. On combining laws (6) and (4) which are the analogs of the laws of Boyle and Charles, there results the more general law that

$$\frac{(P + 39{,}780)}{t + 272.8} F = R_L = 0.1069 \text{ liter-atm.}$$

It is therefore possible to calculate the fluidity of mercury at any temperature and pressure by first reducing the volume to the standard condition of 0° and 760 mm. pressure and then applying law (5). This equation is being worked out for polyatomic molecules.

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[8] Richards, THIS JOURNAL, **48**, 3072 (1926).