Fluidity: A General Theory

J. H. HILDEBRAND AND R. H. LAMOREAUX

Department of Chemistry, University of California, Berkeley, Calif. 94720

Contributed by J. H. Hildebrand, August 5, 1972

ABSTRACT The equation $\phi = B(V - V_0)/V_0$, which reproduces the fluidity of simple liquids accurately over ranges between freezing and boiling points, is here shown to hold to pressures of at least 500 atm, and nearly to critical volumes. Fluidity can vary continuously above the critical region into that of compressed gas, where the parameter B becomes a function of temperature.

The parameter V_0 is a "corresponding states" fraction of the critical molal volume. It is identical with the molal volume of the solid only in cases where molecules are free to rotate as they do in the liquid.

Parameter B is a measure of the extent to which the external momentum that produces viscous flow is absorbed by the molecules of the liquid. Such damping can result from molecular mass, e.g., Ne, Ar, Kr; flexibility, normal alkanes; or rotational inertia, SiBr₄ against SiCl₄.

In a previous paper (1) on *Motions of Molecules in Liquids: Viscosity and Diffusivity*, various evidence was presented showing that the fluidity of a simple liquid, ϕ , at atmospheric pressure and at any temperature, is proportional to the fractional excess of its molal volume, V , over the molal volume, V_0 , at which the molecules are so closely crowded as to prevent viscous flow while still retaining rotational freedom. At volumes less than V_0 only plastic flow is possible. This concept is expressed formally by the equation:

$$\phi = B \frac{V - V_0}{V_0} \quad [1]$$

The unit of viscosity is the "poise." It can be defined in terms of liquid held between a fixed and a moving plate, 1 cm apart; the viscosity is the force in dynes divided by the area of the moving plate that must be applied to it in order to maintain a steady velocity of 1 cm/sec. The moving plate transmits momentum to the molecules of the liquid. Fluidity, in terms of this arrangement, can be thought of as the velocity of the moving plate, in cm/sec, when the force applied is 1 dyne/cm² of area. The viscosity of ordinary liquids at ambient temperatures is of the order of 10⁻² poise; hence, it is customary to use the centipoise as the unit. The unit of fluidity is thus a reciprocal centipoise, cP⁻¹.

The value of V_0 for a liquid is obtained, as explained in ref. 1, by plotting experimental values of ϕ at different temperatures against the values of V , the molal volumes of the liquid, at the same respective temperatures. The scores of simple liquids that we have examined in this way all yield straight lines over ranges of temperature from 0° up nearly to boiling points. Extrapolated to $\phi = 0$, they yield values of V_0 . The slope of a line is $\phi/(V - V_0)$, which is B/V_0 . In the following pages we show that this equation accounts correctly for the fluidity of simple liquids of various types over large ranges of

pressure, volume, and temperature. We explain also that V_0 and B are definite physical quantities, not simply adjustable parameters.

Alkanes

We first apply these concepts to alkanes. Values of V_0 and B , determined from values of viscosity and density found in the literature, are given in Table 1. The values of V_0 for normal alkanes increase linearly with molecular weights. They are also "corresponding states" fractions, 0.300, within limits of error, of critical molal volumes, as far as these are available, as seen in Table 2. One of us (2) recently called attention to the fact that the mean of ratios of molal volumes of 11 simple liquids at their boiling points, V_b , to their critical volumes is 0.377. Accordingly, values of V_0 can be estimated with only moderate uncertainty from 0.796 V_b .

Values of B for normal, branched, and cycloalkanes are plotted in Fig. 1 against the number of carbon atoms in the compound. The most striking feature of such a plot is the straight line for normal alkanes from propane to the longest chains for which data appear trustworthy. We have omitted some badly scattered points for chain lengths above 20, where prediction by linear extrapolation would appear to be much more reliable than published data in this region.

One sees, next, that B -values for cycloalkanes are a little smaller than those of the corresponding normal alkanes, and that those of branched chains are a little larger. Especially noteworthy is the series of the pentanes: *cyclo*-, *normal*-, *iso*-, *neo*-. Although the major factor determining fluidity is the crowding of the molecules, expressed by the ratio $(V - V_0)/V_0$, the absorption of energy during molecular collisions in-

FIG. 1. Variation of the fluidity parameters of alkanes, B , reciprocal centipoises, with number of carbon atoms and molecular structure.

volved in the transfer of momentum, represented by B , can be very significant. It is to be expected that molecules with rotational inertia would lose more energy during collision than molecules with none. This effect may account for the steep drop in B values from CH_4 to C_2H_6 to C_3H_8 . From then on, the normal alkanes can absorb energy by bending, a loss that is proportional to the length of the chain. We present below further evidence on the relation of B -value to molecular composition and structure.

We emphasize that Eq. 1, with the parameters V_0 and B in Table 1, makes it possible to calculate viscosities of normal

TABLE 1. Values of V_0 , cm^3/mol and B , reciprocal centipoise

	V_0	B	Reference
CH_4	32.0	35.5	a
C_2H_6	49.6	25.5	a
C_3H_8	61.0	19.8	a
C_4H_{10}	77.7	19.2	a
C_5H_{12}	94.0	18.7	a
C_6H_{14}	111.0	18.0	a
C_7H_{16}	129.1	17.7	a
C_8H_{18}	146.4	17.0	a
C_9H_{20}	165	16.9	a
$\text{C}_{10}\text{H}_{22}$	183	16.6	a
$\text{C}_{11}\text{H}_{24}$	201	16.0	a
$\text{C}_{12}\text{H}_{26}$	217	15.5	a
$\text{C}_{13}\text{H}_{28}$	238	15.0	a
$\text{C}_{14}\text{H}_{30}$	253	14.0	a
$\text{C}_{15}\text{H}_{32}$	273	14.0	a
$\text{C}_{16}\text{H}_{34}$	291	13.5	a
$\text{C}_{17}\text{H}_{36}$	309	13.1	a
$\text{C}_{18}\text{H}_{38}$	329	13.1	a
$\text{C}_{19}\text{H}_{40}$	345	12.2	a
$\text{C}_{20}\text{H}_{42}$	365	12.2	a
$\text{C}_{24}\text{H}_{50}$	434	9.8	b
$\text{C}_{35}\text{H}_{72}$	622	6.0	b
$\text{c-C}_9\text{H}_{10}$	83.3	17.6	a, c
$\text{c-C}_6\text{H}_{12}$	103.2	17.2	a, d
$\text{c-C}_8\text{H}_{16}$	130.7	12.6	e
$2\text{-CH}_3\text{C}_3\text{H}_7$	82.2	21.3	a
$2,2\text{-(CH}_3)_2\text{C}_3\text{H}_6$	104.4	23.9	a
$2\text{-CH}_3\text{C}_4\text{H}_9$	98.2	20.0	a, f
$2\text{-CH}_3\text{C}_5\text{H}_{11}$	113.5	20.7	f, g
$2\text{-CH}_3\text{C}_6\text{H}_{13}$	131.0	20.7	a, f
$2,2,4\text{-(CH}_3)_3\text{C}_5\text{H}_9$	150.5	19.9	a, h, i
$2\text{-CH}_3\text{C}_7\text{H}_{15}$	148.0	19.0	c
$2\text{-CH}_3\text{C}_{10}\text{H}_{21}$	201	15.9	j

- Rossini, F. D. *et al.* (1971) *American Petroleum Inst. Research Project No. 44*. Carnegie Press, Pittsburgh, Pa.
- Nederbragt, G. W. & Boelhouwer, J. W. M. (1947) *Physica* **13**, 305–318.
- Geist, J. M. & Cannon, M. R. (1946) *Ind. Eng. Chem. Anal. Ed.* **18**, 611–613.
- Friend J. N. & Hargreaves, W. D. (1944) *Phil. Mag.* **35**, 57–64.
- Kuss, E. Z. *Angew. Physik* (1955) **7**, 372–378.
- Thorpe, E. & Rodger, J. W. (8974) *Phil. Trans. Roy. Soc. Lond.* **A185**, 397–710.
- Bridgman, P. W. (1931/32) *Proc. Amer. Acad.* **66**, 185–233.
- Maman, A. (1938) *Comptes Rend.* **207**, 1401–1402.
- Evans, E. B. (1938) *J. Inst. Petroleum Techn.* **24**, 48–53.
- Terres, E. & Brinkmann, L. *et al.* (1959) *Brennstoffchemie* **40**, 279–280.

TABLE 2. "Corresponding States" ratio of V_0 to critical volume for normal alkanes cm^3/mol

	V_c	V_0	(V_0/V_c)
CH_4	99.4	32.0	0.322
C_2H_6	148.1	44.6	0.301
C_3H_8	203.2	61.0	0.300
C_4H_{10}	254.9	77.7	0.305
C_5H_{12}	304.4	94.0	0.309
C_6H_{14}	369.9	111.0	0.300
C_7H_{16}	431.9	129.1	0.299
C_8H_{18}	492.4	146.4	0.297

alkanes from C_3H_8 to chain lengths of 20 or more carbon atoms with accuracy quite equal to that of measured values, and that the role of temperature is simply to determine the magnitude of $(V - V_0)$.

Effect of pressure on fluidity

The viscosity of propane has been determined at pressures up to 544 atm, as shown in Table 3. The constancy of the ratio $\phi/(V - V_0)$ in the last column shows that Eq. 1 accounts excellently for the effect of high pressures upon fluidity.

Tetrahalides and elements

The four tetrachlorides in Table 4 have B values that decrease sharply from CCl_4 to SnCl_4 with increase in size, tetrahedral shape, and moments of rotation that increasingly resist the momentum of viscous flow. The increase in mass from SnCl_4 to SiBr_4 , which have the same V_0 , causes ϕ to drop from 9.0 to 5.5. The decrease in fluidity from 45.2 for Ne to 12.3 for Kr, with Ar_2 between, must result from increasing atomic mass.

It is not possible, because of lack of independent data, to calculate quantitatively the effect upon fluidity of molecular flexibility, softness, and inertia of rotation. In fact, fluidity of liquids itself offers the most significant information to be had about molecular repulsions. The difference between $B = 45.0$ for neon and 22.7 for argon clearly shows how naive it is to use the same inverse 12th-power to express their repulsive potential.

Distinction between V_0 and V_s , the molal volume of the solid

Others have sought to identify V_0 with V_s . This is possible only for substances whose molecules retain rotational energy in the solid state, as do those of CCl_4 ; most species of poly-

TABLE 3. Values of $\phi/(V - V_0)$ for propane at 311°K and different pressures^{a, b}

P, atm	ϕ , cP^{-1}	V , cm^3/mol	$\phi/(V - V_0)$
13.60	11.79	93.3	0.365
68.05	10.46	90.0	0.361
136.1	9.31	87.0	0.358
272.2	7.84	83.0	0.356
544.4	6.21	78.3	0.359

- Reamer, H. H. Sage, B. H. & Lacey, W. N. (1949) *Ind. Eng. Chem.* **41**, 482–484.
- Starling, K. E. Eakin, B. E. & Ellington, R. T. (1960) *AIChE J.* **6**, 438–442.

FIG. 2. Van der Waals paths from liquid to gas along different isotherms.

atomic molecules are able to crystallize in a less symmetrical, nonrotating, denser form of lower energy. In such cases, V_0 can be reached only by undercooling the liquid. *Para*-xylene (3), for example, freezes at 13.2° from $V = 122.5 \text{ cm}^3$ to $V_s = 101.9 \text{ cm}^3$, much smaller than the volume required for free rotation in the liquid, where $V_0 = 114.5 \text{ cm}^3$. *Meta*-xylene whose density, viscosity, and heat capacity are nearly the same as those of *p*-xylene in their common liquid range above 13.2° , cannot freeze into a comparable closely packed solid form, and remains liquid to -47° . Its value of V_0 is 113.5 cm^3 .

Cogwheel molecules

Magill and Ubbelohde (4) have prepared substances, such as tridiphenyl methane, whose molecules have three long arms. They found their viscosities, plotted as $\log \eta$ against $1/T$, gave lines that acquired curvature above the freezing point, an effect that they attributed to "prefreezing." Plotted in our

TABLE 4. Values of V_0 and B for tetrahalides and elements. Units cm^3/mol and cP^{-1}

	V_0	B	Reference
CCl_4	89.9	13.4	a, b
SiCl_4	97.5	12.6	c, d, e
TiCl_4	98.3	10.2	c, f
SnCl_4	104.7	9.0	c, g
SiBr_4	104.9	5.5	c, h
Ne	14.3	45.2	i, j
Ar	24.5	22.7	i, j
Kr	29.0	12.3	i, j

- Billings, B. H. & Gray, D. E. Eds., *American Institute of Physics Handbook* (McGraw-Hill, New York, 1963).
- Young, S. (1910) *Sci. Proc. Roy. Dublin Soc.* **12**, 374-443.
- Lutshinsky, G. P. (1937) *J. Gen. Chem. (USSR)* **7**, 2116-2127.
- Bowden, S. T. & Morgan, A. R. (1940) *Phil. Mag.* **29**, 367-378.
- Hölemann, P. (1936) *Z. Physik. Chem.* **B32**, 353-368.
- Sagawa, T. (1933) *Sci. Rep. Tōhoku Univ.* **22**, 959-971.
- Ulich, H. Hertel, E. & Nespital, W. (1932) *Z. Physik. Chem.* **B17**, 369-379.
- Nisel'son, L. A. Sokolova, T. D. & Lapidus, I. I. (1967) *Zh. Neorg. Khim.* **12**, 1423-1426.
- Förster, S. (1963) *Cryogenics* **3**, 176-179.
- Agrawal, G. M. & Thodos, G. (1971) *Phys. Chem. Fluids* **2**, 135-145.

FIG. 3. Variation of fluidity from liquid to gas at different temperatures and pressures.

way as ϕ against V , such substances give lines that curve to the left as ϕ approaches 0. Their arms become entangled as $(V - V_0)$ approaches 0. Fluidity increases more slowly when $(V - V_0)$ is small than when it is large. We have found this bending of the line in the case of $(\text{C}_4\text{F}_9)_3\text{N}$. It surely is not caused by "prefreezing." Hildebrand and Archer (3) showed that *meta*- and *para*-xylenes have nearly the same liquid molal volumes through their common liquid range, and Smith and Hildebrand (5) found almost identical viscosities, with no evidence of "prefreezing" of the *para*-isomer above its melting point, 13.2° .

Liquid metals also obey Eq. 1, but we are not able to account for their individual B -values.

Fluidity in the transition from liquid to gas

The linearity observed for plots of ϕ against V for simple liquids below their boiling points made us curious to find out how far it would continue at higher temperatures and volumes.

In order to prevent evaporation, it is necessary to increase pressure, after which expansion can continue along different

TABLE 5. Parameters for C_2H_8 and CO_2 . Volumes, cm^3/mol

	T_c	V_c	V_0	B	Reference
C_2H_8	370	203.2	61.0	19.8	a, b, c
CO_2	304	94.0	25.2	11.0	d, e, f, g

- Rossini, F. et al., *American Petroleum Institute Research Project No. 44* (Carnegie Press, Pittsburgh, 1953).
- Reamer, H. H. Sage, B. H. & Lacey, W. N. (1949) *Ind. Eng. Chem.* **41**, 482-484.
- Starling, K. E. Eakin, B. E. & Ellington, R. T. (1960) *AIChE J.* **6**, 438-442.
- Stakelbeck, H. (1933) *Z. Ges. Kälteind* **40**, 33-40.
- Handbook of Chemistry and Physics*, 42nd Ed. (Chemical Rubber Co., Cleveland, 1961), p. 2465.
- Kestin, J. Whitelaw, J. H. & Zien, T. F. (1964) *Physica* **30**, 161-181.
- Michels, A. Botzen, A. & Schuurman, W. (1957) *Physica* **23**, 95-102.

FIG. 4. Plots of ϕ against $T^{1/2}$ at $V = 0.60, 1.20$, and 20 liters.

isotherms, as depicted in the van der Waals-type plot of Fig. 2, paths *b*, *c*, and *d*. If the pressure applied is not sufficient to surmount the critical region, ϕ can travel discontinuously along path *a*.

Let us see how ϕ varies as V increases along these different paths. Data for propane and carbon dioxide are plotted in Fig. 3. Significant properties for these compounds are given in Table 5. (Note that the B -value of CO_2 , with rigid, linear molecules, is much smaller than that of the more-symmetrical C_3H_8 .) The lines below the critical region are quite straight, although ϕ increases to 30 reciprocal centipoise, cP^{-1} , ten times its value for liquids below their boiling points. As V is further increased, the fluidity begins to depend strongly upon the temperature chosen. We explain the effect of temperature as follows: at the critical temperature, V_c is only $2.65 V_0$, but as volume increases, the molecules acquire translational momentum increasing in proportion to $(V^{1/3} - V_0^{1/3})$, up to

its kinetic theory value, $(3mkT)^{1/2}$. This random momentum offers resistance to the vector momentum imposed when viscosity is measured; therefore, ϕ varies inversely with $T^{1/2}$, as seen in Fig. 4 for propane. This relation for dilute gases is well known from kinetic theory (4). The departure in the critical region is not unexpected. The difference between a pair of lines in Fig. 3 increases in parallel with increases in $(V^{1/3} - V_0^{1/3})$. We are not ready to reduce this physical description of the process to precise mathematical terms.

NOTE ADDED IN PROOF

Eicher, L. D. & Zwolinski, B. J. (1972) *Science* **177**, 369, stated that Eq. 1 of this paper does not adequately agree with data for viscosity of *n*-hexane, *n*-decane, *n*-heptadecane, and *l*-pentanol. They arrive at this conclusion by an analytical application of least squares.

The degree of agreement between theory and experiment is usually revealed far more clearly in a suitable plot than from an analytical application of the method of least squares. In the case of hexane, for example, a plot of ϕ against V of the data referred to in Table 1a, whose temperatures range from 70° to -90° , plotted on a 50-cm scale fall on a straight line with scarcely perceptible deviations. Indeed, the values of B and V_0 for the scores of liquids given in this paper have all been obtained from such straight-line plots.

This work has been supported by the National Science Foundation and by the Petroleum Research Fund of the American Chemical Society.

1. Hildebrand, J. H. (1971) *Science* **174**, 490-493.
2. Hildebrand, J. H. (1969) *Proc. Nat. Acad. Sci. USA* **64**, 1331-1334.
3. Archer, G. & Hildebrand, J. H. (1961) *Proc. Nat. Acad. Sci. USA* **47**, 1881-1882.
4. Magill, J. H. & Ubbelohde, A. R. (1958) *Trans. Faraday Soc.* **54**, 1811-1821.
5. Smith, E. B. & Hildebrand, J. H. (1964) *J. Chem. Phys.* **40**, 909-910.