Free Volume Theory for Viscosity of Simple Nonpolar Liquids

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Part I. Pure Components

An improved free volume theory is presented, and is shown to predict the variation of viscosity with temperature and pressure satisfactorily for liquids composed of simple, nonpolar molecules, when the density is greater than twice the critical value. Allowance is made for the temperature dependence of the minimum free volume for a jump, and for the density dependence of the activation energy at constant volume. Corresponding states relationships are provided for these quantities, the reducing parameters being the temperature and molal volume at the melting point.

For densities up to about the critical value, transport properties of simple fluids may be predicted with reasonable accuracy by either the empirically modified Enskog equations (*1* to *3*), or correlations based on the residual viscosity concept (*4*). Neither of these approaches are able to describe transport property behavior at densities in the normal liquid region (roughly $\rho \geqq 2\rho_c$), nor do they predict the change in sign of $(\partial\eta/\partial T)_\rho$ that is observed experimentally at densities of about $2\rho_c$ (*5* to *7*).

At present the activation and free volume theories for liquid transport properties seem to represent the most promising approach for a simple method of predicting transport properties in the normal liquid density region. Such theories are analogous to the free volume theories for liquid thermodynamic properties, but the former take account of the possibility of molecules leaving their cells.

Features of previous theories due to Eyring (*8*), Weymann (*9*, *10*) and Cohen and Turnbull (*11*, *12*) have recently been combined by Macedo and Litovitz (*13*). Molecular flow is presumed to occur only if a combination of two criteria are met. Firstly the molecule must possess an energy greater than some critical value e_v, termed the activation energy at constant volume, and secondly a fluctuation must occur such that the local free volume is greater than a critical value v_0. The viscosity free volume referred to here represents the space unoccupied by molecules, and should not be confused with the quantity termed free volume in thermodynamic theories. The resulting equation is

$$\eta = A \exp\left(\frac{V_0}{V - V_0}\right) \exp\left(\frac{E_v}{RT}\right) \qquad (1)$$

Chung (*14*) has presented an elegant derivation of Equation (1). Various workers disagree as to the correct form for the pre-exponential factor. Most have predicted that A varies with $T^{1/2}$, and such a temperature dependence is assumed in this work. Equation (1) has been shown to correlate the viscosity data for various liquids (*13*) including polymeric materials (*15*), the parameters A_o, V_o, and E_v being treated as adjustable constants for each molecular species. The equation is not very successful when applied in this way to viscosity and self-diffusivity data of molecularly simple liquids (*16*, *17*).

The purpose of this paper is to test the suitability of Equation (1) for predicting the viscosity behavior of simple, pure liquids. In a subsequent paper the theory is extended to liquid mixtures.

THE PARAMETER V_0

If the molecules behave as rigid spheres, V_0 for any substance should be a constant independent of temperature and density, as assumed by Macedo and Litovitz (*13*). For real fluids one expects V_0 to be independent of density, but to decrease somewhat with increasing temperature, because as temperature rises the average kinetic energy of the molecules increases, and molecules are thus able to approach each other more closely. Such temperature dependence should be most evident for simple molecules, as the repulsive portion of their intermolecular potential energy curve rises less steeply than for more complex polyatomic molecules.

To obtain an expression for this temperature dependence the molecules are assumed to obey the $(6, n)$ pair potential law (*19*):

$$\phi(r) = \epsilon K\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6\right] \qquad (2)$$

The parameter n indicates the steepness of the repulsive part of the curve; for small molecules such as the inert gases n is close to 12, whereas for more complex molecules the best value of n is 28 or higher. Equating the average

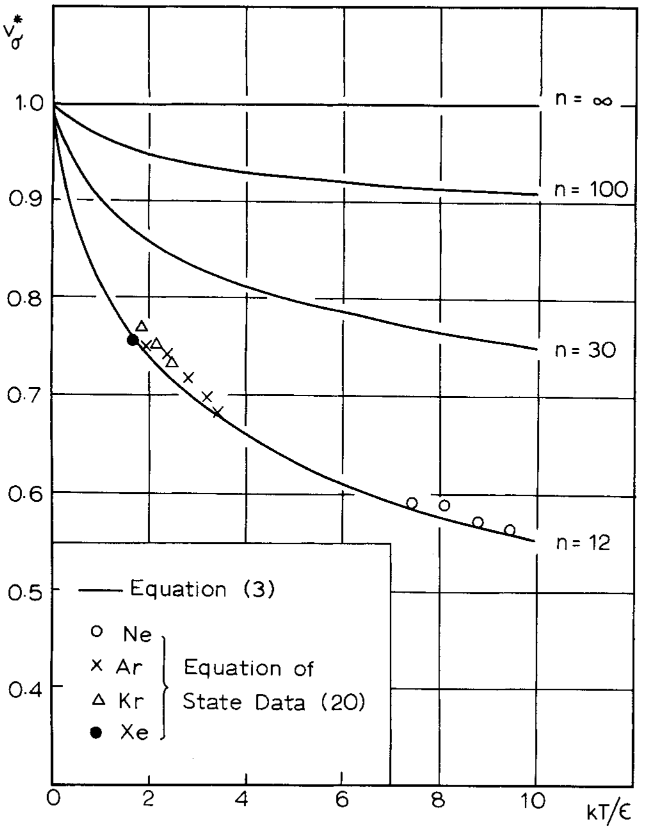

Fig. 1. Variation of v_σ^* with T^* from Equation (3).

kinetic energy of a two-molecule system to the potential energy of the system at the distance of closest approach, d:

$$3kT = \epsilon K\left[\left(\frac{\sigma}{d}\right)^n - \left(\frac{\sigma}{d}\right)^6\right]$$

or, in reduced form

$$3T^* = K\left[\left(\frac{1}{v_\sigma^*}\right)^{n/3} - \left(\frac{1}{v_\sigma^*}\right)^2\right] \qquad (3)$$

Equation (3) may be solved to obtain v_σ^* as a function of T^* for various n values. The resulting temperature dependence is shown in Figure 1. Since V_o should be determined primarily by molecular size, we assume

$$V_o = \zeta\ v_\sigma^*$$

where ζ is a constant for a particular molecule, and V_o at any temperature can be calculated from

$$V_o = V_o^1 \cdot \frac{v_\sigma^*}{v_\sigma^*(T^* = 1)} \qquad (4)$$

Thus a knowledge of V_o^1, together with n and ϵ, suffices to calculate V_o at any temperature from Figure 1. Support for the above procedure is provided by values of the hard-sphere diameter calculated at various temperatures from equation of state data for inert gases by Dymond and Alder (*20*). These are included in Figure 1, and agree well with the curve for $n = 12$.

The parameter V_o^1 should be related in some way to molecular size, and if suitably reduced the resulting dimensionless minimum free volume may be quite constant for a series of similar molecules. Because free volume theories apply best at high densities, the molal volume at the melting point seems a more appropriate reducing parameter than the critical volume. Thus

$$V_o^* = \frac{V_o^1}{V_m} \qquad (5)$$

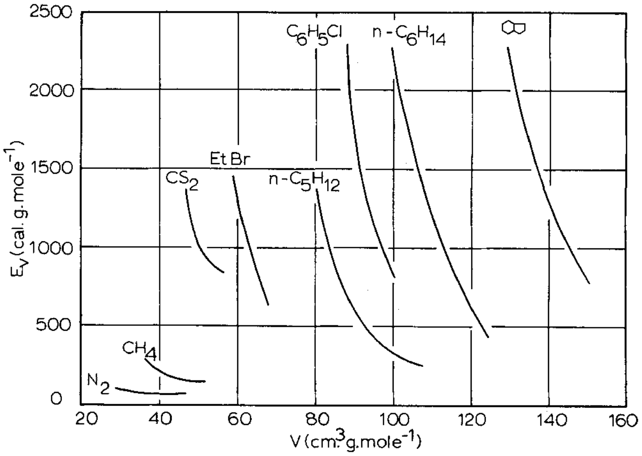

Fig. 2. Activation energy at constant volume.

THE PARAMETER E_v

From Equations (1), (3), and (4)

$$\frac{E_v}{R} = \lim_{T\to 0}\left[\frac{\partial \ln(\eta/T^{1/2})}{\partial T^{-1}}\right]_v \qquad (6)$$

so that E_v may be calculated from experimental viscosity values. For the more complex molecules where n is large (for example, benzene) a plot of $\ln(\eta/T^{1/2})$ vs. $1/T$ is found to be approximately linear, and the requirement $T \to 0$ in Equation (6) is less stringent. As pointed out by Brummer (*21*), E_v should vary with density. A strong density dependence is found on applying Equation (6) to experimental data, and is shown in Figure 2.

The activation energy arises when the jumping molecule moves from its initial equilibrium position through a region of higher potential energy to its final position. A model of the situation is shown in Figure 3 in which a molecule

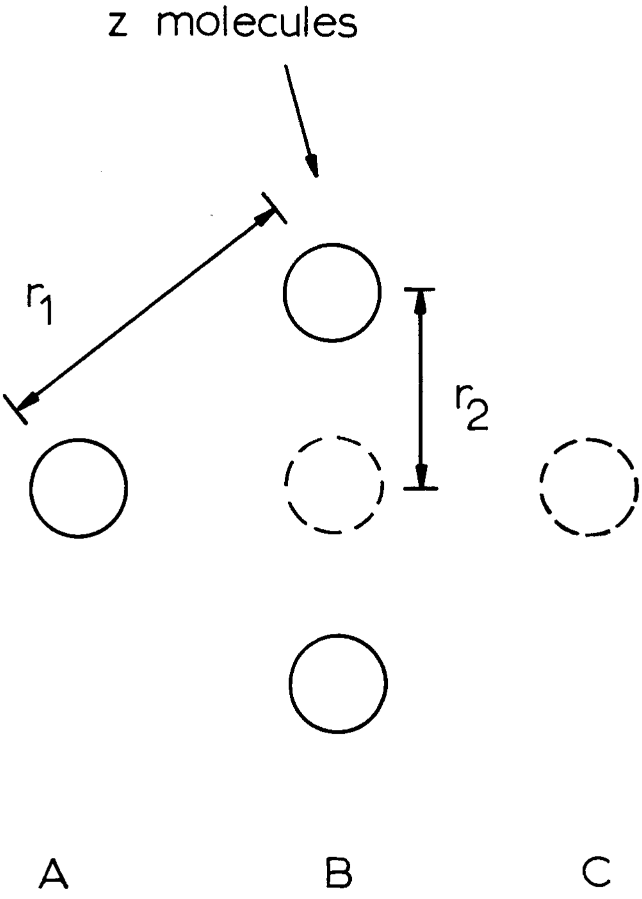

Fig. 3. Model of a jump.

jumps from A to C, and passes through a region B where it has to squeeze through a ring of z molecules. The activation energy may be written

$$e_v = z\,[\phi(r_2) - \phi(r_1)]$$

$$= Kz\epsilon\left[\left(\frac{\sigma}{r_2}\right)^n - \left(\frac{\sigma}{r_2}\right)^6\right] - Kz\epsilon\left[\left(\frac{\sigma}{r_1}\right)^n - \left(\frac{\sigma}{r_1}\right)^6\right]$$

Then

$$e_v = KzkT_m\psi^{-1}\left\{\left[\left(\frac{\delta v_m}{\beta v}\right)^{n/3} - \left(\frac{\delta v_m}{\beta v}\right)^2\right] - \left[\left(\frac{\delta v_m}{v}\right)^{n/3} - \left(\frac{\delta v_m}{v}\right)^2\right]\right\} \quad (7)$$

For a group of similar molecules the constants β, δ, z, ψ, and n should be approximately the same, and the above expression suggests the corresponding states relation

$$E_v^* = E_v^*(V^*) \quad (8)$$

where the reduction is performed with melting parameters. Such a corresponding states plot is shown in Figure 4 for nonpolar molecules. Good agreement is obtained at high reduced volumes, but some scatter is observed at lower values of V^*, where the curve rises steeply. This may be attributed to differences in n for molecules within the group. Viscosity data used were taken from Bridgman (*22*) and from references given in Table 1.

TABLE 1. DATA SOURCES AND RANGE OF CONDITIONS

Molecule	Temperature range (°K.)	Molal volume range (cc. mole^{-1})	Density ref.	Viscosity ref.	No. of points
Ne	28 to 38	17 to 21	*23*	*24, 25*	7
Ar	90 to 270	29 to 39	*5, 26*	*5, 16, 23, 27*	26
Kr	115 to 125	34 to 35	*28*	*28*	4
Xe	162 to 323	44 to 54	*28, 29*	*28, 29*	7
N_2	70 to 106	32 to 47	*6, 30*	*6, 30*	12
O_2	81 to 148	27 to 45	*28, 30*	*31, 32*	10
CO	69 to 81	33 to 35	*28, 30*	*28, 31*	6
CH_4	97 to 165	36 to 48	*28, 30*	*28, 32, 33*	8
CD_4	93 to 115	36 to 38	*28*	*28*	5

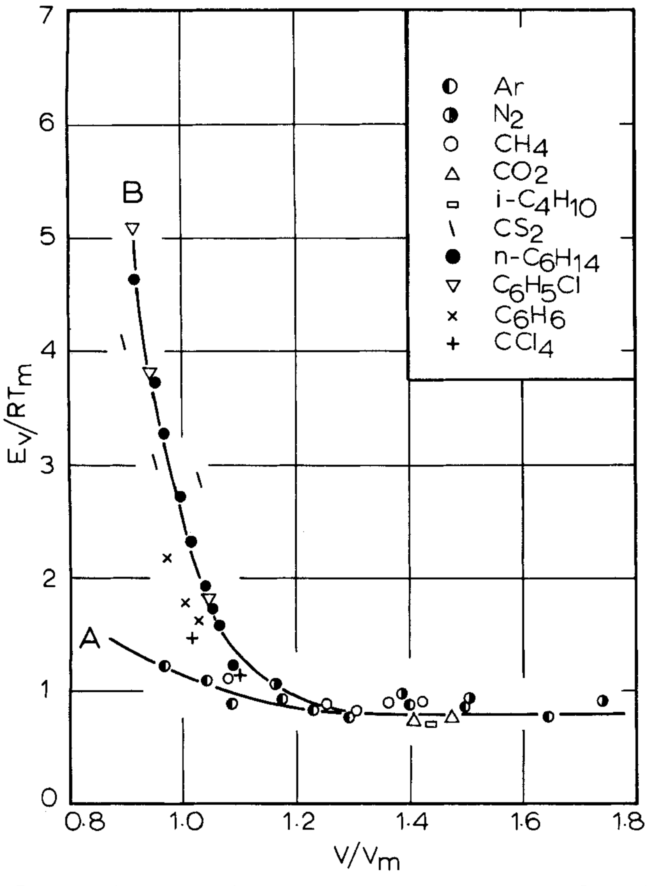

Fig. 4. Reduced plot of activation energy against volume. Curve A is for simple molecules obeying a Lennard-Jones (6, 12) potential. Curve B shows an approximate relationship for more complex molecules (large *n* values).

COMPARISON WITH EXPERIMENT

Attention is here restricted to simple molecules for which the Lennard-Jones 6, 12 intermolecular potential law should be a reasonable approximation. Such a group may include the inert gases and most diatomic molecules, and perhaps methane. In order to perform a rigorous test of the theory, viscosity data over as wide a range of conditions as possible is desirable. The only monatomic and diatomic liquids for which viscosity data are available over a wide range of density as well as temperature seem to be argon and nitrogen, for which Zhdanova (*5*, *6*) has reported extensive measurements. The range of experimental conditions used corresponds to pressures up to several thousand atmospheres. The accuracy of the experimental argon data appear to be of the order 6% over the entire range of conditions, but the nitrogen data are in poorer agreement with measurements of other workers, and the accuracy appears to be of the order 12 to 15%. To test the theory for these two liquids, and to establish the corresponding states relationships in Equations (5) and (8) the following procedure was adopted:

1. The experimental data were plotted as $\ln(\eta/T^{1/2})$ vs. T^{-1} at constant volume. Values of E_v were estimated at various volumes from the lines extrapolated to low temperature, using Equation (6).
2. Values of the parameters A_o and V_o^1 were obtained from a best fit to the viscosity data using the computer, Equations (3) and (4) being used to obtain the temperature dependence of V_o.

Theory and experiment are compared for argon in Figure 5. Similar agreement between theory and experiment is found for nitrogen, with $V_o^1 = 17.0$ cc./mole and $A_o = 2.53 \times 10^{-5}$ poise (°K.)$^{-1/2}$. The theory provides a satisfactory fit to the data for densities above approximately twice the critical value. Thus theory is in error for molal volumes of 39.15 cc./mole and above for argon, and of

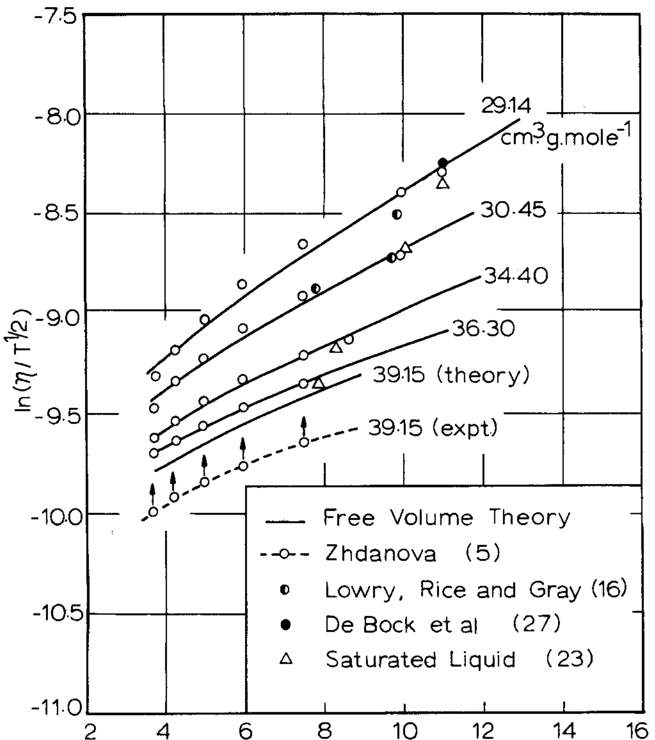

Fig. 5. Test of free volume theory for argon. $V_0^1 = 16.2$ cc. (g.mole)$^{-1}$ $A_o = 2.53\times10^{-5}$ poise (°K.)$^{-1/2}$.

TABLE 2. PARAMETERS FOR MOLECULES STUDIED

Molecule	V_o^1 (cc. mole^{-1})	10^5A_o (poise. °K.$^{-1/2}$)	ϵ/k (°K.)	T_m (°K.)	V_m (cc. mole^{-1})	V_c (cc. mole^{-1})	$\frac{A_oV_m^{2/3}}{M^{1/2}}\cdot 10^5$	Avg. % Error
Ne	8.95	2.52	35.7	24.57	16.2	41.7	3.59	2.9
Ar	15.5	2.65	124	83.2	28.0	75.2	3.87	4.7
Kr	19.0	3.10	190	116.2	34.3	92.2	3.57	0.5
Xe	24.6	3.48	229	161.2	44.3	118.8	3.80	2.5
N_2	17.8	2.53	91.5	63.1	32.2	90.1	4.85	5.5
O_2	13.5	3.91	113	54.8	24.3	78	5.81	5.3
CO	18.3	2.54	110	68.1	33.1	93.1	5.06	2.5
CH_4	19.5	1.59	148	90.7	35.2	99	4.26	2.7
CD_4	19.5	1.77	146	89.8	35.1	99	4.24	1.3

56.0 cc./mole and above for nitrogen. The density range in which the theory applies is sharply defined, and is similar to that in which similar models for thermodynamic properties, such as the Prigogine smoothed potential model (*18*), apply. The theory appears to apply for temperatures below about $1.5T_c$, although the region of satisfactory temperature dependence is less clearly defined.

The values of the parameters E_v and V_o^1 found for argon and nitrogen may be used to form the basis of corresponding states correlations of these parameters, as described in previous sections, from which values for other molecules may be predicted. The average value of the reduced minimum free volume for argon and nitrogen is 0.554, so that

$$V_o^* = \frac{V_o^1}{V_m} = 0.554 \qquad (5a)$$

To test the correlation for simple liquids, values of V_o were calculated from Equations (3), (4), and (5*a*), assuming $n = 12$, and taking values of ϵ/k determined from gas viscosity data (*19*). Values of E_v were found using curve A of Figure 4. The best values of A_o were obtained by substituting experimental viscosity data in Equation (1) for each molecule. For most of the molecules other than argon and nitrogen few data are available at high pressures, and most of the viscosity data used were for the saturated liquid. Tables 1 and 2 show the data sources and parameters for each of the molecules studied.

The average percentage deviation between experiment and theory is about 6% or less. This seems to be of the same order as the accuracy of the experimental viscosity data for these liquids. The data of Zhdanova (*6*) for nitrogen at high pressures seems to be in poor agreement with that of other workers (*30*), and saturated liquid viscosity data (*30*) were used in obtaining the A_o value given in Table 2 for this molecule.

Figures 6 and 7 compare experimental and predicted viscosities for xenon and methane. The predicted values become less reliable as the density falls to values approaching $2\rho_c$ (for methane this corresponds to V = 49.5 cc./mole).

The expressions for the pre-exponential factor A_o proposed by Eyring (*8*) and Weymann (*9*) are

Eyring

$$A_o = (2\pi mk)^{1/2}\frac{v_f^{1/2}}{v}$$

Weymann

$$A_o = \frac{3}{4}(2\pi mk)^{1/2}\left(\frac{1}{v^{2/3}}\right)$$

These expressions suggest that the group $(A_oV_m^{2/3}/M^{1/2})$

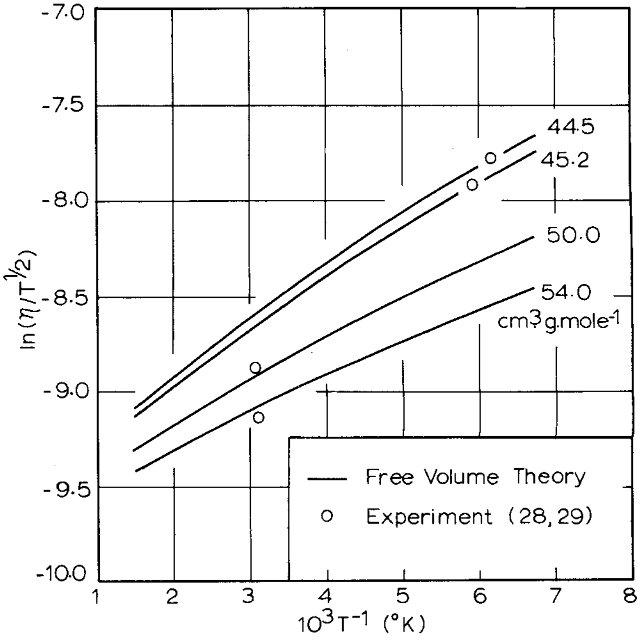

Fig. 6. Viscosity of xenon.

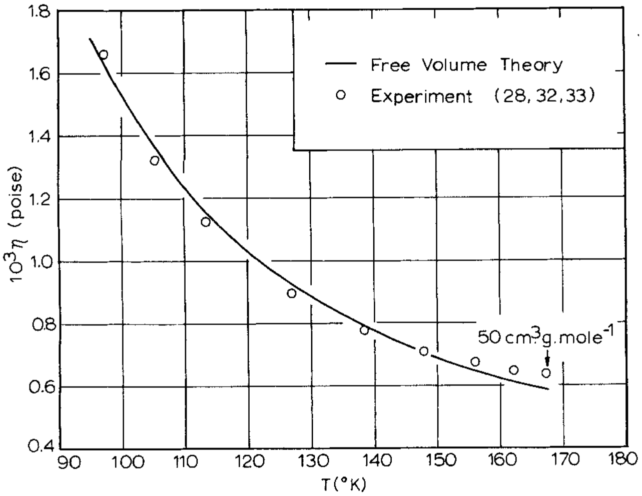

Fig. 7. Viscosity of saturated liquid methane.

may be approximately the same for different molecules. Values shown in Table 2 indicate that this quantity is approximately constant for inert gas liquids, but for the other molecules a range of values is found. Apparently the above expressions for A_o are not generally valid, and cannot form the basis of a successful corresponding states relationship for this parameter. In general an experimental value of the viscosity is needed to determine A_o for a given molecule; this can be used together with the proposed correlations for V_o and E_v to predict viscosity values at other temperatures and densities.

CONCLUSIONS

By allowing for the variation of V_o with temperature it is possible to account quantitatively for the nonlinearity of constant volume plots of $\ln(\eta/T^{1/2})$ vs. T^{-1} for simple liquids. The physical model predicts a density dependence of E_v, and thus explains the variation with density of the slope of constant volume plots of $\ln(\eta/T^{1/2})$ vs. T^{-1}. With these improvements the free volume theory is able to describe the viscosity behavior of liquids composed of simple, nonpolar molecules that may be expected to approximately obey a Lennard-Jones 6, 12 potential law.

The fact that both $V_o{}^1$ and E_v values vary in a corresponding states way indicates that the free volume theory provides a reasonably correct picture of viscosity behavior for these liquids, and shows that the equation's success does not arise only from the availability of three adjustable parameters. The simple expressions given for A_o by Eyring and others, however, do not seem to be generally applicable.

The free volume equation provides a useful basis for predicting viscosities of simple liquids at high densities, where most other correlations are unsuccessful. It should be possible to obtain similar correlations for more complex molecules, provided groups of molecules obeying approximately the same potential law are chosen. In such cases the corresponding states relations obtained for E_v and $V_o{}^1$ would be expected to differ somewhat from those for liquids obeying a simple 6, 12 potential law.

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NOTATION

A = pre-exponential factor
A_o = $A/T^{1/2}$
d = distance of closest approach of two molecules
E_v = activation energy per mole
$E_v{}^*$ = E_v/RT_m
e_v = activation energy per molecule
K = $(n/n-6)\ (n/6)^{6/(n-6)}$
k = Boltzmann constant
M = molecular weight
m = mass of molecule
n = repulsive exponent in (6, n) potential
R = gas constant
r = distance separating two molecules
T = temperature
T^* = kT/ϵ
V = volume per mole = $\tilde{N}\,v$
V^* = V/V_m
V_c = critical molal volume
V_m = melting volume
V_o = minimum free volume per mole needed for molecular flow to occur = $\tilde{N}\,v_o$
$V_o{}^*$ = $V_o{}^1/V_m$ = reduced minimum free volume
$V_o{}^1$ = value of V_o when $T^* = 1$
v = average volume per molecule
v_f = average free volume per molecule
v_o = minimum free volume per molecule needed for molecular flow to occur
$v_\sigma{}^*$ = $(d/\sigma)^3$
$v_\sigma{}^*(T^* = 1)$ = value of $v_\sigma{}^*$ when $T^* = 1$
z = number of nearest neighbors in ring

Greek Letters

α = $(v/r_1{}^3)$ = constant
β = $(r_2/r_1)^3$ = constant
δ = $(\alpha\sigma^3/v_m)$ = constant
ϵ = energy parameter in (6, n) potential
ζ = constant
η = viscosity
ρ = density
ρ_c = critical density
σ = distance parameter in (6, n) potential
ϕ = intermolecular pair potential energy
ψ = kT_m/ϵ = constant

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Part II. Mixtures

The free volume equation for liquid viscosities is generalized to multicomponent mixtures. No experimental mixture data are needed in order to use the correlation. Calculated viscosities for liquid mixtures composed of molecules which approximately obey the Lennard-Jones 6, 12 potential law show very good agreement with experimental data for eight binary systems.

A method of estimating the viscosity of liquid mixtures should represent an extension of a satisfactory treatment of pure liquids (*1*), and its use should require only pure component data. In Part I of this work (*2*), the viscosity equation (1) proposed by Macedo and Litovitz (*3*) was shown to predict viscosities of simple liquids for $\rho \geqq 2\rho_c$, provided that allowance was made for the temperature dependence of V_o and for the volume dependence of E_v. In this part the theory is extended to mixtures. As before, attention is restricted to liquids composed of simple, nonpolar molecules, whose potential interactions may be expected to approximately obey the Lennard-Jones 6, 12 law.

MIXING RULE FOR E$_V$

A mixture containing molecular species 1, 2, ... i, j .... r is assumed. The simple model of a molecular jump used for pure components in part I is used here for mixtures (Figure 3 of part I), with the following additional assumptions:

1. The molecules are randomly mixed. This assumption is known to be a good approximation for many simple liquid mixtures (*4*).
2. The intermolecular distances r_1 and r_2 are independent of the molecular species involved. However, these distances will vary with composition as the molal volume changes.

Consider a molecule of species i in the process of making a jump. The most probable number of molecules of type j contained in the ring of surrounding molecules will be $x_j z$, using assumption 1. The activation energy is

$$e_v{}^i = \sum_{j=1}^{r} x_j e_v{}^{ij}$$

where

$$e_v{}^{ij} = z\,[\phi_{ij}(r_2) - \phi_{ij}(r_1)] \tag{1}$$

and $\phi_{ij}(r)$ is the intermolecular potential energy for an $i - j$ pair at a separation r. The fraction of such jumps that involve molecules of type i is x_i, so that the average activation energy for the mixture is

$$e_v = \sum_{i=1}^{r} x_i e_v{}^i = \sum_{i=1}^{r} \sum_{j=1}^{r} x_i x_j e_v{}^{ij}$$

$$E_v = \sum_i \sum_j x_i x_j E_v{}^{ij} \tag{2}$$

When $i = j$ the terms $E_v{}^{ij}$ are those for the pure components and they may be estimated by methods previously described (*2*). The cross-terms $E_v{}^{ij}$ arise from unlike pair