Self-Diffusion in Liquids

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In a recent paper by Dullien (1972), an accurate expression for self-diffusion in liquids was presented. An equivalent expression may be developed from a consideration of the rigid sphere developments of Longuet-Higgins and Pople (1956).

For self-diffusion, based on the exponential decay of the autocorrelation function for the velocity of a particle, Longuet-Higgins and Pople presented the expression

$$D = \frac{l}{2}\sqrt{\frac{\pi kT}{m}}\;\frac{1}{z-1} \tag{1}$$

It will be remembered that a similar expression has been developed by Enskog [see Chapman & Cowling (1952)] who applied dilute gas theory to liquids by correcting for finite molecular volumes and the increased frequency of molecular collisions.

Longuet-Higgins and Pople similarly found that the shear viscosity of a rigid sphere fluid at high densities could be expressed as

$$\eta = \frac{4Nl}{5V}\sqrt{\frac{mkT}{\pi}}\;(z-1) \tag{2}$$

In their development of Equation (2) they assumed that the pair distribution function of relative position is independent of the rate of strain and that the velocity distribution is locally Maxwellian.

Combining Equations (1) and (2), rearrangement and setting $\rho = M/VN$ gives

$$\frac{D\eta M}{l^2\rho} = \frac{2}{5}RT \tag{3}$$

This equation has been shown to be a good basis for the development of liquid metal predictive equations [Vadovic and Colver (1970, 1971)].

The compressibility of a rigid sphere fluid has been described by an expression developed by Carnahan and Starling (1969)

$$z = \frac{1+y+y^2-y^3}{(1-y)^3} \tag{4}$$

where

$$y = \frac{4}{3}\,\frac{\pi N l^3}{V} \tag{5}$$

Ashcroft and Lekner (1966) as well as Ascarelli and Paskin (1967) have pointed out that the transition from solid to liquid occurs at $y_m = 0.45$ for metals. Carnahan and Starling (1969) suggest a value of $y_m = 0.48$ to 0.49 for argon. Thus, combining Equations (5) and (3) and setting $y_m = 0.45$ gives

$$\frac{D\eta M}{\rho T} = 0.106 \times 10^{-8}\, V_m^{2/3} \tag{6}$$

The plot of Equation (6) in Figure 1 for a number of substances, the data of which may be found in Dullien (1972), Vadovic and Colver (1970), and O'Reilly and Peterson (1972) indicates that, indeed, a linear relationship holds; however, a least square fit of the data indicates that the coefficient should be approximately twice that value given in Equation (6). The empirically adjusted result is

$$\frac{D\eta M}{\rho T} = 0.216 \times 10^{-8}\, V_m^{2/3} \tag{7}$$

This equation represents the self-diffusion data in Figure 1 with an average error of less than 6%.

Alternately, Dullien presented for the self-diffusion coefficient the semi-empirical expression

$$\frac{D\eta V}{RT} = 0.124 \times 10^{-16}\, V_c^{2/3} \tag{8}$$

It has been shown that the liquid volume at the melting point V_m is directly proportional to the critical volume V_c. In fact this proportionality has been shown by Vadovic and Colver (1972) to be closely approximated by

$$V_m = 0.310\, V_c \tag{9}$$

The equivalence of Equations (8) and (7) can now be shown by combination of Equations (8) and (9) to give

$$\frac{D\eta V}{RT} = 0.219 \times 10^{-8}\, V_m^{2/3} \tag{10}$$

The advantages of using the form of the expression represented by Equations (7) or (10) are apparent on considering a liquid metal or other high boiling substances in which critical volume are not generally available. However density data for most liquids are available, and the melting point density and hence the melting point volume can easily be determined.

NOTATION

D = self-diffusion coefficient
l = atomic radius
m = atomic mass
z = rigid sphere compressibility

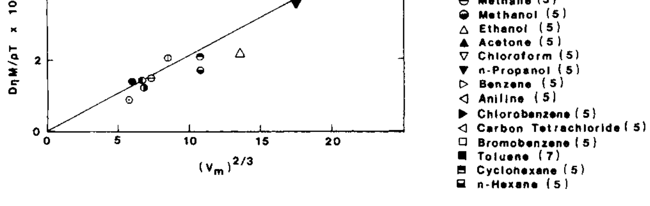

Fig. 1. Plot of $D\eta M/\rho T$ vs. $(V_m)^{2/3}$ for pure liquids.

k = Boltzmann's constant
T = absolute temperature
N = Avogadro's number
V = atomic volume
η = shear viscosity
M = molecular weight
R = gas constant = Nk
ρ = density
y = reduced density = $b/4V$
b = molecular covolume = $\frac{16}{3}\pi N\sigma^3$

Subscripts

m = melting point
c = critical

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A Note on the Equilibrium Partial Pressures of Vapors Above Sulfuric Acid Solutions

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The equilibrium partial pressures of sulfuric acid, sulfur trioxide, and water above aqueous solutions of sulfuric acid are of interest in several areas of chemical engineering. Applications for this information are found in the sulfuric acid industry itself, in industries which use sulfuric acid, and in the fuel industry where the dew point of sulfur-containing flue gases may be determined by the above described equilibrium. There are essentially two methods of obtaining this needed information, that is, the partial pressures can be directly measured or they can be calculated from other measurements using the principles of thermodynamics. This note points out some of the difficulties of calculating this equilibrium from other thermodynamic data and compares these calculated predictions with the available experimental data on vapor pressures.

THEORETICAL CONSIDERATIONS

Abel (1946) and Gmitro and Vermeulen (1964) have *made the only published attempts to estimate the partial* pressures of sulfuric acid, sulfur trioxide, and water above aqueous solutions of sulfuric acid. Abel based his estimates of the partial pressures of sulfuric acid and water upon the pure component enthalpy and entropy change during vaporization as well as liquid activity data and extrapolation of the reaction equilibrium data of Bodenstein and Katayama (1909) from 325°C down to 25°C. At the time that Gmitro and Vermeulen made their estimates, similar pure component data and the more detailed liquid-and- gas-phase data of Giauque (1960) and Giguere (1963), respectively, were available.

In general, the partial pressures of sulfuric acid and water are estimated from an equation of the following form:

$$\ln p_i = A_i(x, T) \tag{1}$$

In this equation, i represents either water or sulfuric acid and A_i is a function of liquid concentration and temperature. Normally, this function is written in the following form:

$$A_i(x, T) = a_i + b_i \ln(T) + c_i(1/T) + d_iT + e_iT^2 \tag{2}$$