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CORRESPONDENCE

Liquid Diffusivities

SIR: Liquid diffusivities are involved in the correlation and interpretation of the performance data on equipment that effects a transfer of a material to or from a liquid phase as in liquid-liquid extraction, absorption, distillation, and leaching. None of the theoretical approaches have yielded equations that can predict this diffusivity with satisfactory accuracy. Wilke (4) has expressed the liquid diffusivities in an equation of the form derived by Eyring (1, 2) based on the theory of absolute reaction rates. This equation approaches the Stokes-Einstein equation for large molecules and requires the introduction of an empirical constant evaluated from a family of curves. The reference curve was developed for the wide range of data on water, and the other curves were arbitrarily constructed parallel to this curve at one end and approaching it at the other end. These curves were based on a limited range of data, and certain inconsistencies in the data can be noted. The parameter of the curves decreased to 0.7 as the molecular volume of the solvent increased to about 100. However, in order to handle the data on miscellaneous solvents available in the literature (most of which had this molecular volume or higher), Wilke recommended a parameter of 0.9 as giving the most probable value of the diffusivity.

It is possible to express Wilke's correlation by the empirical equation

$$F = 1.22 \times 10^7 \frac{V_A^{1/3}}{1 + \left(\frac{3V_B}{V_A}\right)^{2/3}} \qquad (1)$$

The value of F so determined is used to calculate the diffusivity according to the equation

$$D = \frac{1}{F} \frac{T}{\mu} \qquad (2)$$

Equation 1 is in perfect agreement with Wilke's curve for water over the entire range of the data, but the equation approaches the theoretical $1/3$ slope required by the Stokes-Einstein equation at a slower rate than Wilke's extrapolated curve, so the equation gives values about 10% higher at solute volumes of 3000. No data are available in this region and the uncertainty of extrapolation was noted by Wilke in showing a dashed curve in this region.

Equation 1 also shows perfect agreement with Wilke's curve for methanol solvent over most of the range of the data and the calculated values for benzene as the solvent passes through the bulk of the data, but it gives lower values than Wilke's curve at low solute volumes while all the observed data lie above his curve in this region.

As the molecular volume of the solute approaches that of the solvent or becomes smaller, the mechanism for diffusion changes. In the case of water, Equation 1 holds to $V_A = V_B$ and thereafter, if the value of the denominator is retained constant at this maximum value, the single point of data for hydrogen agrees with the calculated diffusivity. In the case of methanol, Equation 1 holds to $V_A = 1.5 V_B$ without deviation. This represents the smallest value of V_A for which data are available, and more data are required to establish the lower limit with this solvent.

On the other hand, data for benzene solutions hold to $V_A = 2V_B$, and then by maintaining the denominator constant at this value, the points at the lower values of V_A that lie above Wilke's curve can be calculated correctly.

The data on other miscellaneous solvents agree with the equation if the denominator is maintained at some maximum value between $V_A = 2V_B$ and $V_A = 3V_B$. As an average value, the equation may be assumed to hold to $V_A = 2.5 V_B$, and then the denominator may be maintained constant at this maximum value of 2.13 for the miscellaneous solvents.

There is no theoretical reason for the denominator to remain constant at low values of V_A; but since all the available data in this region consist of one or two scattered points, it is impossible to empirically develop any theory. The investigation of the diffusivities of small molecules in solvents of large molecules may lead to better understanding of the theory of the liquid state.

The complete equation for liquid diffusivity from Equations 1 and 2 becomes

$$D = 8.2 \times 10^{-8} \frac{T}{\mu} \frac{1 + \left(\frac{3V_B}{V_A}\right)^{2/3}}{V_A^{1/3}} \qquad (3)$$

This equation appears to represent the behavior of large molecules in dilute solution diffusing through a solvent of small molecules, and appears to correct adequately for the effect of the solvent volume down to a solute volume equal to about twice the solvent volume, although in some solvents the range may extend down to solute volumes equal to the solvent volumes. It also gives better agreement with the original correlation than the equation suggested by Sherwood and Pigford (3) which deviates from the correlation at solute volumes below 40.

NOMENCLATURE

D = diffusion coefficient, sq. cm./sec.
F = diffusion factor = $T/D\mu$
T = absolute temperature, ° K.
V = molecular volume used by Wilke (4)
μ = viscosity of solution centipoises

Subscripts

A = solute
B = solvent

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Viscosity of Gases

Sir: Recently Bromley and Wilke (1) proposed a method for calculating the viscosity of gases at low pressures that employed the tables of collision integrals calculated by Hirschfelder, Bird, and Spotz (3) based on the kinetic theory of Chapman and Cowling (2). Their basic equation was

$$\mu = 0.0026693 \left[\frac{1}{r_0^2} \sqrt{\frac{ME}{k}} \right] \left[f\left(\frac{kT}{E}\right) \right] \tag{1}$$

where the second bracketed term represents the values of the function of kT/E that must be read from the tables. They also noted that for values of kT/E between 10 and 400, the function could be represented by a simple exponential equation. This corresponds to reduced temperatures between 5 and 200, and for lower temperatures, which are more common, the individually tabulated values are required.

This table can be reduced to a simple equation by examining the deviations from the exponential equation which applies to the higher range. The equation that has been developed for the function is

$$f\left(\frac{kT}{E}\right) = 0.879 \left(\frac{kT}{E}\right)^{0.645} - 0.261 \left(\frac{kT}{0.7E}\right)^{-0.9 \, \log \frac{kT}{0.7E}} \tag{2}$$

The equation is accurate within 1 in the third significant figure down to values of kT/E of 0.5 which is within the accuracy of slide rule calculation. However, at the lower values, the equation gives the function as the difference between two large numbers; and thus the error increases rapidly from less than 1% at kT/E equal to 0.4, to 6% at kT/E equal to 0.3. This was the lowest value given in the table by Bromley and Wilke (1) and corresponds to T_r of about 0.225 so it is outside the usual range of engineering calculation.

Hirschfelder, Bird, and Spotz (3) gave empirical methods for estimating E/k and r_0 for gases

$$E/k = 0.75 \, T_c \tag{3}$$

$$r_0 = 0.833 \, V_c^{1/3} \tag{4}$$

from which Bromley and Wilke (1) derived the relationship

$$\mu = \frac{0.00333 \, \sqrt{MT_c}}{V_c^{2/3}} \, f\left(\frac{kT}{E}\right) \tag{5}$$

which when combined with Equation 2 in terms of the reduced temperature according to Equation 3 becomes

$$\mu = \frac{\sqrt{MT_c}}{V_c^{2/3}} [0.00352 \, T_r^{0.645} - 0.00087 \, (1.9 \, T_r)^{-0.9 \, \log (1.9 T_r)}] \tag{6}$$

Bromley and Wilke had reported an average deviation of 4.4% for their equation for 45 gases and since no calculatable errors are introduced by Equation 2, the final one or Equation 6 should show the same agreement, and is applicable to values of T_r greater than 0.3.

The equation thus eliminates the need for the large table of values and thus provides a more convenient application of Bromley and Wilke's original equation.

NOMENCLATURE

k = Boltzman constant, ergs/° K.
M = molecular weight
r_0 = collision diameter
T = absolute temperature, ° K.
V = volume, cc.
E = energy difference between molecules
μ = gas viscosity centipoise

Subscripts

c = critical conditions
r = reduced condition

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