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Atomic test of the Stokes-Einstein law. II. Diffusion of Xe through liquid hydrocarbons

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The diffusion coefficient D has been measured for ^{133}Xe atoms diffusing through 12 liquid n-alkanes, n-pentane through n-hexadecane, at 20.0 °C. The dependence of D (cm^2/sec) on the viscosity η (P) was found to be $D=(1.26\pm0.06)\times10^{-6}\eta^{-0.686\pm0.011}$ where $\eta_{20.0\,^\circ\mathrm{C}}$ varies monotonically in these solvents from 0.235 cP (for n-C_5H_{12}) to 3.48 cP (for n-$C_{16}H_{34}$). The observation that D is proportional to η to a negative power of magnitude near $\frac{2}{3}$ is in agreement with other work on several different solute-solvent systems. Some ramifications of this dependence are suggested.

I. INTRODUCTION

Understanding diffusion of molecules in liquids is important for fundamental problems in statistical mechanics and liquids. It is equally important for basic and applied problems in biology and chemistry since many processes are diffusion limited.

In this paper we report a diffusion measurement which is prototypical in the following sense: Xenon, the solute, is monatomic and inert. The solvents, n-alkanes from n-pentane (n-C_5H_{12}) through n-hexadecane (n-$C_{16}H_{34}$), form a homologous series of liquids whose properties change gradually. Finally, the method of measuring the diffusion coefficient D (cm^2/sec) is a direct application of its definition as flux per unit-concentration gradient.

This experiment is a natural extension to simpler systems of a previous measurement of D for Xe through water-sucrose solutions.[1] In those solvents, which have two components and are polar, it was observed that D depended on the viscosity η of the solvent according to $D\propto\eta^{-0.63\pm0.02}$.[1] In this experiment, using one-component nonpolar solvents, we observed a similar dependence, namely, $D\propto\eta^{-0.686\pm0.011}$.

What is expected for the diffusion of small particles and noninteracting molecules through liquids? If the diffusing particles are large and massive compared to the solvent's molecules, for example, Brownian particle diffusion, then the Stokes-Einstein (SE) law applies:[2]

$$D=k_BT/6\pi\eta R\ . \tag{1}$$

In Eq. (1), T is the absolute temperature, η is the viscosity of the solvent, and R is the radius of the diffusing particle. Because the denominator of Eq. (1) comes from a formula of Stokes[3] which holds for macroscopic particles in a continuous fluid and is derived from the Navier-Stokes equations[4] one might expect that the SE law would only hold for such particles. In fact, however, Eq. (1) holds over a wide range of small particle size, even to diffusion of small polyatomic molecules. The SE law holds for self-diffusion of liquid tetramethylsilane,[5] benzene,[5] and methanol.[6] In these applications the denominator of Eq. (1) must be changed to $4\pi\eta R$ to account for slip boundary conditions. Some of these phenomena may be understood from molecular statistical-mechanical considerations[7,8] and from generalized hydrodynamics and molecular dynamics.[9,10]

In general the Stokes-Einstein law in the form of Eq. (1) does not apply for microscopic diffusion. However, in many atomic and molecular systems D still depends in a simple way on the solvent viscosity, i.e., $D\propto1/\eta^p$.[11–14] This is important because (a) it gives insight into the meaning of the macroscopic quantity η for microscopic kinetics of diffusion, and (b) it may make possible predictions of D, which are especially important for applications, based on empirical rules as well as fundamental principles. Our work is in that spirit; if there is a simple relation between D of a microscopic solute and η of the solvent, then one might expect it to show up in simple systems such as ours.

Xenon has several properties which justify its use as a prototype solute. The atoms are inert and spherical with completed electronic p shells. The interatomic force between Xe atoms is a weak, short-range van der Waals force, which can be well described by a Lennard-Jones potential.[15,16] Partly because of this, Xe and the other inert-gas elements have been studied extensively, theoretically, and experimentally, as prototype solids and liquids. A lot is therefore known about their interactions and properties.[15–17]

A principal idea in the choice of solute and solvents in the present experiment is that since we have Xe atoms interacting with nonpolar solvent molecules, the solute-solvent interaction potential should be relatively easy to model. We imagine the Xe atom as a sphere of diameter about 4.5 Å interacting with a sea of CH_2 (and some CH_3) groups bonded to each other. The C—C bond length in the n-alkanes is about 1.5 Å. Since the solute-solvent forces are probably also weak and short range, the interaction of Xe with n-alkane molecules will not change much over this series of solvents, i.e., the local environment of a Xe atom in liquid n-C_5H_{12} is approximately the same as that in n-$C_{16}H_{34}$. There is experimental evidence for this in our recent measurements of the solubility of Xe in n-alkanes.[18,19] We also found similar conditions in n-alkanols,[20] where the solvent molecules are polar. If a theory of molecular diffusion in liquids can be approached from first principles, then one might expect it to apply to systems like the present ones.

Diffusion of Xe through organic liquids is important for several practical applications. The radioactive isotope ^{133}Xe is used in nuclear medicine to study cerebral blood flow and pulmonary disease; in this application one measures effects in body fluids and tissues of diffusion and solubility of Xe. Xenon is also used for research as a prototype inhalational general anesthetic[21] and to study the mechanism of general anesthesia. Since some of the lighter *n*-alkanes are anesthetics as well, our work involves anesthetic-anesthetic interactions.[22] Inert-gas diffusion and solubility are important for studying decompression sickness and inert-gas narcosis in deep-sea diving.[23] Finally radioactive inert gases, especially ^{133}Xe and ^{85}Kr, are important components of the inventory of nuclear reactors so that their diffusion and solubility properties are useful for control of emissions during normal operation and in reactor accidents.[24,25]

II. EXPERIMENTAL

The experimental technique and apparatus are essentially the same as in some of our previous diffusion work.[1,26] All these experiments use the radioactive isotope ^{133}Xe, which is commercially available.[27] This isotope emits 81-keV γ rays (half-life 5.27 days), which can be detected and counted straightforwardly. To obtain a measure of the concentration of ^{133}Xe in a given volume as a function of time we measured the radiation intensity (in our case counts/400 sec), which is proportional to the concentration, at ten-minute intervals using a suitable fixed geometry. Figure 1 shows a schematic scale drawing of the principal parts of the apparatus used to make these diffusion measurements. It has not been shown previously.

In Fig. 1, V_1 and V_2 are glass vials (each about 12 cm^3) which serve respectively as the source and sink for ^{133}Xe flow. These volumes originally contain air at 1 atm. To start the experiment one puts a charge of order 0.1 μCi of ^{133}Xe into V_1 and joins serially together V_1, the glass capillary, and V_2. The vials are sealed with epoxy into Al blocks which have been suitably drilled out so that the ^{133}Xe diffuses from V_1 to V_2 through a column of liquid alkane (length l, cross-sectional area A) which is contained in the capillary. Column length is monitored during the experiment with a remote cathetometer. In order to minimize vibrations and thermal convection in the liquid, the entire apparatus is in a quiescent constant-temperature bath which is itself isolated in an external temperature-controlled bath at 20.0 °C.

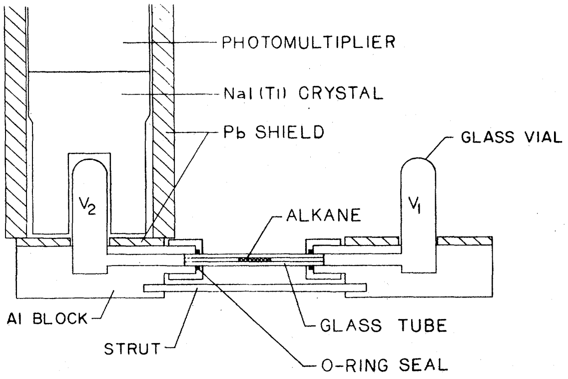

FIG. 1. Schematic scale diagram of diffusion apparatus.

The source and sink vials fit with essentially identical geometries into the well of a single shielded scintillation detector which is a NaI(Tl) crystal attached to a photomultiplier. The shielding is designed so that the detector measures radiation only from the vial upon which it is mounted. We normally measure the radioactivity from V_1 briefly at the beginning and at the end of a run and we measure the radioactivity from V_2 essentially continuously during the course of the run.

Initially upon charging V_1 with ^{133}Xe there is no ^{133}Xe in the liquid. However, if one waits a time $\tau_0 \geq (l^2/\pi^2 D)\ln 100$, then the concentration gradient of ^{133}Xe in the liquid column is almost constant,[1,28] and one can then analyze the data using Fick's law. For these experiments τ_0 ranged from about 4 to 25 h where one estimates D conservatively before the run.

If $N_1(t)$ and $N_2(t)$ are, respectively, the numbers of ^{133}Xe atoms in V_1 and V_2, then Fick's equations are[1]

$$\frac{dN_1}{dt} = -\frac{DLA}{l}\left[\frac{N_1}{V_1}-\frac{N_2}{V_2}\right] - \lambda N_1 , \tag{2}$$

$$\frac{dN_2}{dt} = -\frac{DLA}{l}\left[\frac{N_2}{V_2}-\frac{N_1}{V_1}\right] - \lambda N_2 . \tag{3}$$

The exact solution for $N_2(t)$ may be written

$$N_2(t)e^{\lambda t} = [N_2(0) - N_0 V_e/V_1]\exp-(DLAt/lV_e) + N_0 V_e/V_1 . \tag{4}$$

In these equations $\lambda = 0.9134\times 10^{-4}$ min^{-1} is the decay constant, $V_e = V_1V_2/(V_1+V_2)$, N_0 is the total ^{133}Xe initially present in the system, and t is measured from τ_0. Since the Ostwald solubility L of Xe in the liquid solvent is the ratio of the number density of Xe atoms in the liquid to that in the gas, the average concentration gradient which drives the diffusion across the liquid is $(L/l)(N_1/V_1 - N_2/V_2)$ in Eq. (2). This means that this technique gives unavoidably a measure of the product DL and not of D alone. By combining our data with independent measurements of L for Xe in n-alkanes,[19] we computed D values.

One may linearize Eq. (4) by expanding the exponent and neglecting higher-order terms. This gives the final form

$$N_2(t)e^{\lambda t} = N_2(0) + [N_0V_e/V_1 - N_2(0)](DLA/lV_e)t . \tag{5}$$

Equation (5) shows that under the assumptions a plot of $N_2(t)e^{\lambda t}$ *versus* t gives a straight line and that DL can be determined from its slope. The maximum fractional error in D due to linearizing Eq. (4) is $\Delta D/D \approx DLAt_{\max}/2!lV_e$. Under our experimental conditions this quantity was small (average 1.2%).

Figure 2 is a plot of a typical set of data. They were taken on a column of n-$C_{10}H_{22}$ about 1.2 cm long and

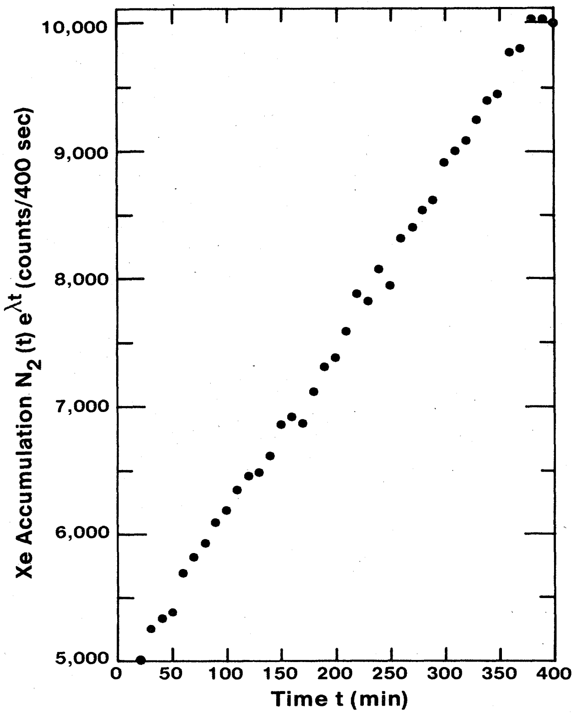

FIG. 2. Time course of the accumulated concentration of ^{133}Xe on the sink side of the diffusion apparatus for a typical run. In this case the liquid through which the diffusion took place was a column of *n*-decane (at 20.0 °C) about 1.2 cm long in a capillary of 0.33 cm i.d. The ordinate has been normalized by the factor $e^{\lambda t}$ ($\lambda = 0.9134 \times 10^{-4}$ min^{-1}) to account for radioactive decay.

0.09 cm^2 in cross section. The ordinate $N_2(t)e^{\lambda t}$ is actually radiation intensity observed during the run while the detector was mounted, as shown in Figure 1, on V_2. The abscissa on Fig. 2 is the time elapsed starting $\tau_0 \approx 7\frac{1}{3}$ h after the sides were joined and $N_2(0)$, accumulated during τ_0, is about 5000 counts/400 sec. During the 400 min duration of the run there was an additional accumulation in $N_2(t)e^{\lambda t}$ of about 5000 counts/400 sec.

In all, we made 25 determinations of D at 20.0 °C for these 12 *n*-alkanes. Typical uncertainty in D was about 4.2%; the largest contributions to the uncertainty are from the slopes of $N_2(t)e^{\lambda t}$, the cross-sectional areas, and the solubilities. As a test that the results were independent of the geometry of the diffusion barrier we used varying lengths l from about 0.6 to 2.2 cm and we used two different capillaries with diameters 0.20 and 0.33 cm. In practice V_1 and V_2 must be corrected to include the gas volumes in the Al blocks and in the capillary. It is useful to moisten the inner walls of V_1 and V_2 with a small amount of the alkane since this keeps down the evaporation of volatile liquids from the column itself.

It is also interesting that one could obtain D and L independently from the complete time course of $N_2(t)$ and $N_1(t)$ starting from the time the sides are joined but the analysis is more difficult. To do this one starts with the diffusion equation

$$\frac{\partial c(x,t)e^{\lambda t}}{\partial t} = D \frac{\partial^2 c(x,t)e^{\lambda t}}{\partial x^2} ,$$

where $c(x,t)$ is the concentration of ^{133}Xe in the liquid column, and solves it subject to appropriate boundary and initial conditions.

III. RESULTS AND DISCUSSION

The averaged results of all our measurements of diffusion coefficients at 20.0 °C for ^{133}Xe through *n*-alkanes are shown in Table I. Ostwald solubilities L (20.0 °C) for ^{133}Xe in these solvents, which were used in calculating D values from the data, range from 5.48 for *n*-pentane to 3.14 for *n*-hexadecane. They are given in Table I of Ref. 19.

Many diffusion coefficients for tracer diffusion in polyatomic liquids have recently been measured by Evans, Tominaga, and Davis[12] and by Chen *et al.*[13,14] These workers used a Taylor dispersion technique and worked in a wide temperature range, viz., 25–160 °C. Their values at 25 °C which may be compared with our values in Table I are D(Xe in *n*-hexane) = $(5.44 \pm 0.04) \times 10^{-5}$ cm^2/sec, D(Xe in *n*-octane) = 4.06×10^{-5} cm^2/sec, D(Xe in *n*-decane) = $(2.86 \pm 0.03) \times 10^{-5}$ cm^2/sec, and D(Xe in *n*-tetradecane) = $(1.72 \pm 0.01) \times 10^{-5}$ cm^2/sec.[12,14] The two sets of results are in better agreement for the longer than for the shorter alkanes, even though one expects D to increase with temperature.[14] Shorter *n*-alkanes have higher vapor pressures and lower surface tensions compared to longer *n*-alkanes. This affects the length measurement and meniscus of the liquid columns in our technique and may contribute to the discrepancy. There is a recent corresponding states treatment of gas diffusion in alkanes.[29]

Figure 3 shows results in the form of D versus η. Each point represents one of the 25 determinations of D that we made. The dashed line is the linear regression fit to the logarithmic plot of these data; its equation is

$$D = (1.26 \pm 0.06) \times 10^{-6} / \eta^{0.686 \pm 0.011} , \qquad (6)$$

with D in cm^2/sec and η in P. Viscosities η (20.0 °C) of the *n*-alkanes were taken from standard tables.[30] These viscosities increase monotonically as one goes through the 12 liquids we used, from 0.235×10^{-2} P for *n*-pentane at the left of Fig. 3 to 3.484×10^{-2} P for *n*-hexadecane at the right, so that it is clear from the figure which alkane is associated with any point.

TABLE I. Averaged results of measurements of diffusion coefficient D in cm^2/sec for ^{133}Xe diffusing through liquid *n*-alkanes at 20.0 °C. The uncertainty in the D values is about 4.2%.

Alkane	D (cm^2/sec)	Alkane	D (cm^2/sec)
n-C_5H_{12}	7.96×10^{-5}	*n*-$C_{11}H_{24}$	2.52×10^{-5}
n-C_6H_{14}	6.71×10^{-5}	*n*-$C_{12}H_{26}$	2.29×10^{-5}
n-C_7H_{16}	5.54×10^{-5}	*n*-$C_{13}H_{28}$	1.91×10^{-5}
n-C_8H_{18}	4.53×10^{-5}	*n*-$C_{14}H_{30}$	1.67×10^{-5}
n-C_9H_{20}	3.75×10^{-5}	*n*-$C_{15}H_{32}$	1.45×10^{-5}
n-$C_{10}H_{22}$	3.05×10^{-5}	*n*-$C_{16}H_{34}$	1.27×10^{-5}

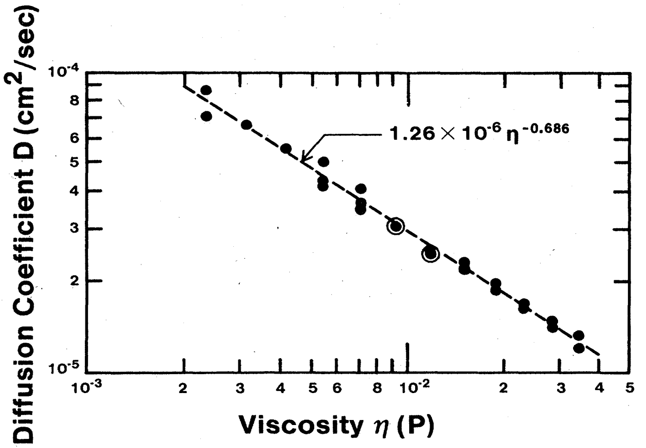

FIG. 3. Experimental results for the diffusion coefficient at 20.0 °C for ^{133}Xe through each of the liquid n-alkanes from pentane through hexadecane. Viscosities of these n-alkanes increase monotonically starting with n-C_5H_{12} ($\eta_{20\,^\circ\mathrm{C}}=0.235$ cP) at the left and going to n-$C_{16}H_{34}$ ($\eta_{20\,^\circ\mathrm{C}}=3.48$ cP) at the right. The dashed line is $D=1.26\times10^{-6}/\eta^{0.686}$, with D in cm^2/sec and η in P.

There have been several measurements of $D(\eta)$ in different systems for which an expression of the form $D(\eta)=A/\eta^p$ was sought. The previous experiment which motivated the present one was a measurement of D (20.0 °C) for ^{133}Xe through water-sucrose solutions using the same technique as here.[1] The result of that experiment was

$$D(\text{Xe in } H_2O+\text{sucrose}) = (7.40\pm0.39)\times10^{-7}/\eta^{0.632\pm0.017}\,, \tag{7}$$

using the same units as Eq. (6), in which the viscosity range was from 1.0×10^{-2} P (for pure water) up to 2.9 P (for an aqueous solution 68% sucrose by weight). It seems remarkable to us that the exponents of η in Eqs. (6) and (7) are similar even though the diffusion systems are so different. Besides the difference in the viscosity ranges in the two systems, as given above, the Ostwald solubility of Xe in the aqueous solutions ranges from 0.11 (for pure water) down to 0.034 (68% sucrose by weight), i.e., much smaller than for Xe in the alkanes as given at the beginning of this section.

There are also important differences in the microscopic environment of the diffusing Xe atom in the systems of Eqs. (6) and (7). For the alkane case, the Xe diffuses through a homogeneous, one-component liquid. For the case of Xe diffusing through water-sucrose solutions, the Xe atom interacts with two components, viz., H_2O molecules and sucrose molecules. Solubility measurements in water-sucrose solutions showed that L (20.0 °C) for Xe is proportional to the volume fraction of water,[1] i.e., the effect of sucrose on solubility was to exclude its volume from that available to Xe.

Equations (6) and (7) suggest that D may be proportional to $\eta^{-2/3}$ and in fact Hiss and Cussler[11] have suggested that as a general result for a small solute diffusing in a large solvent. The actual systems they investigated were n-hexane diffusing through several hydrocarbon solvents and naphthalene diffusing through the same hydrocarbon solvents all at 25 °C with viscosities ranging from 0.5×10^{-2} to 50 P. Their results for viscosity dependence were $D\eta^{0.66}=\text{const}$ for hexane and $D\eta^{0.69}=\text{const}$ for naphthalene. They also plotted (Fig. 3 of Ref. 11) data of several earlier experiments on D versus η at 25 °C in a large variety of systems. They observed that the data fall near a line with a slope of $-\frac{2}{3}$ for viscosities larger than about 5×10^{-2} P. They also suggest a rationalization of this exponent based on the Eyring rate theory.

Recent extensive studies of tracer diffusion in polyatomic liquids, discussed above,[12–14] have generated a lot of data which can be used to test the correlation equation $D\eta^p=\text{const}\times T$. This work showed that p and the constant may be calculated largely from properties of the solute.[14] In particular they use the form $p=-a/r+b$, where r is a solute radius and "p is less than 1 and decreases with decreasing solute radius." A value of $p=0.56$ has been given for Xe.[12] With these considerations they can describe large amounts of diffusion data as functions of η and T.[14]

In conclusion, the Stokes-Einstein law in the form of Eq. (1) does not describe the data in these experiments. The data can however be described by Eq. (6) in which $D=A/\eta^p$ and $p=0.686\pm0.011$. (a) If one assumes that the coefficient p equals $\frac{2}{3}$, and that D is a function only of η, T, R, and the solute mass m, then one is led by dimensional analysis to the relation

$$D=C\frac{(k_BT)^{5/6}}{(mR^2)^{1/6}\eta^{2/3}}\,, \tag{8}$$

in which C is a dimensionless constant. If there were available enough accurate data one could test the validity of Eq. (8). (b) If $D=A/\eta^p$, and especially if p equals $\frac{2}{3}$ or some other "simple" rational number, then that would suggest that there may be some microscopic diffusion parameter which is quantitatively related to the macroscopic η of the solvent. We could then ask, from what properties or features of the microscopic environment of the diffusing particle could the viscosity be quantitatively obtained? The data also suggest that D may be proportional to $\eta^{-2/3}$ for some ideal case but that in real systems one observes perturbations of p about this value.

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[1] G. L. Pollack, Phys. Rev. A **23**, 2660 (1981).

[2] A. Einstein, *Investigations on the Theory of the Brownian Movement,* edited by R. Fürth (Dover, New York, 1956).

[3] G. Stokes, Trans. Cambridge Philos. Soc. **9**, 5 (1856).

[4] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959).

[5] H. J. Parkhurst, Jr. and J. Jonas, J. Chem. Phys. **63**, 2698 (1975); *ibid.* **63**, 2705 (1975).

[6] J. Jonas and A. Akai, J. Chem. Phys. **66**, 4946 (1977).

[7] T. Keyes and I. Oppenheim, Phys. Rev. A **8**, 937 (1973).

[8] J. R. Mehaffey and R. I. Cukier, Phys. Rev. Lett. **38**, 1039 (1977); Phys. Rev. A **17**, 1181 (1978).

[9] B. J. Alder and W. E. Alley, Phys. Today **37(1)**, 56 (1984) and references cited there.

[10] J. J. Brey and J. Gómez Ordóñez, J. Chem. Phys. **76**, 3260 (1982).

[11] T. G. Hiss and E. L. Cussler, AIChE J. **19**, 698 (1973).

[12] D. F. Evans, T. Tominaga, and H. T. Davis, J. Chem. Phys. **74**, 1298 (1981).

[13] S. H. Chen, H. T. Davis, and D. F. Evans, J. Chem. Phys. **75**, 1422 (1981).

[14] S. H. Chen, H. T. Davis, and D. F. Evans, J. Chem. Phys. **77**, 2540 (1982).

[15] G. L. Pollack, Rev. Mod. Phys. **36**, 748 (1964).

[16] *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1976), Vol. I; *ibid.* (Academic, London, 1977), Vol. II.

[17] *Simple Dense Fluids,* edited by H. L. Frisch and Z. W. Salsburg (Academic, New York, 1968).

[18] G. L. Pollack, J. Chem. Phys. **75**, 5875 (1981).

[19] G. L. Pollack and J. F. Himm, J. Chem. Phys. **77**, 3221 (1982).

[20] G. L. Pollack, J. F. Himm, and J. J. Enyeart, J. Chem. Phys. **81**, 3239 (1984).

[21] P. Seeman, Pharmacol. Rev. **24**, 583 (1972).

[22] D. A. Haydon and B. M. Hendry, J. Physiol. **333**, 393 (1982).

[23] *The Physiology and Medicine of Diving and Compressed Air Work,* 2nd ed., edited by P. B. Bennett and D. H. Elliott (Baillière, Tindall, London, 1975).

[24] C. O. Kunz and C. J. Paperiello, Science **192**, 1235 (1976).

[25] G. L. Pollack, U.S. Nuclear Regulatory Commission, Accession No. 8008190073 (September 1979); *ibid.* Accession No. 8004160039 (March 1980).

[26] G. L. Pollack, Biophys. J. **19**, 49 (1977).

[27] Medi Physics, Inc., Plainfield, N.J. 07080.

[28] M. H. Jacobs, *Diffusion Processes* (Springer, New York, 1967), pp. 61–63.

[29] S. H. Chen, AIChE J. **30**, 481 (1984).

[30] *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44* (Carnegie, Pittsburgh, 1953), Table 20c.