10 $= H_2CO_3$
11 $= CaOH^+$
12 $= Ca^{++}$
13 $= CaSO_3{}^0$
14 $= CaSO_4{}^0$
15 $= CaCO_3{}^0$
16 $= CaHCO_3{}^+$
17 $= MgOH^+$
18 $= Mg^{++}$
19 $= MgSO_3{}^0$
20 $= MgSO_4{}^0$
21 $= MgCO_3{}^0$
22 $= MgHCO_3{}^+$
23 $= NaOH^0$
24 $= Na^+$
25 $= NaSO_4{}^-$
26 $= NaCO_3{}^-$
27 $= NaHCO_3{}^0$
28 $= Cl^-$

LITERATURE CITED

Beveridge, G. S. G., and R. S. Schechter, *Optimization: Theory and Practice*, McGraw-Hill, N. Y. (1970).

Bromley, L. A., "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, **19**, 313 (1973).

Epstein, M., L. Sybert, S. C. Wang, and C. C. Leivo, "EPA Alkali Scrubbing Test Facility: Limestone Wet Scrubbing Test Results," *EPA Contract No. Ph22-68-67, NTIS No. 232-359/AS* (1974).

Han, S. T., and L. J. Bernardin, "Ion Activity Coefficients of Sodium Bicarbonate," *Tappi*, **41**, 540 (1958).

Hooke, R., and T. A. Jeeves, "Direct Search Solution of Numerical and Statistical Problems," *J. Assoc. Computer Machines*, **8**, 212 (1961).

Lowell, P. S., D. M. Ottmers, D. M. Strange, K. Schwitzgebel, and D. W. DeBerry, "A Theoretical Description of the Limestone Injection-Wet Scrubbing Process," Vol. I, (NAPCA Contract No. CPA 22-69-138), NTIS No. PB 193-029 (1970).

Manuscript received May 14, 1975; revision received November 25 and accepted November 28, 1975.

Long Range Attractive Forces for Hydrogen-Light Hydrocarbon Pairs

HSUAN TIEN, THOMAS NENNER, and J. B. FENN

Department of Engineering and Applied Science
Yale University, New Haven, Connecticut 06520

Some of the pathways which connect the macroscopic properties of gaseous systems with the dynamics of binary encounters between their constituent molecules have been traveled frequently in both directions. Even so, there remain unknown stretches along the most familiar trails, and prospective routes for most polyatomic molecular systems have not been traversed in even one direction. Not long ago, Chu, Chappelear, and Kobayashi (1975) analyzed experimental data on diffusivity, viscosity, and second virial coefficients for binary mixtures of hydrogen with methane, ethane, propane, and *n*-butane. By a fitting procedure they determined best values of the molecular interaction parameters ϵ/k and σ for specifying both a Lennard-Jones (12-6) potential and a modified Buckingham (Exp-6) potential. For the third parameter (repulsive steepness) of the latter they assumed a value of 12. They then computed the transport and virial properties from these potentials for a number of specific conditions and found good agreement between the calculated and experimental values, usually less than 1% difference. They concluded that in most cases the Exp-6 potential provided somewhat more accurate predictions than the L-J (12-6) potential.

We have been determining absolute values of total cross sections for the scattering of molecular beams of argon atoms by a variety of aliphatic hydrocarbon molecules. By the so-called Schiff-Landau-Lifshitz (1956, 1959) approximation it is possible to determine from the total cross section Q_t the Van der Waals coefficient C_6 of the inverse sixth power term which describes the long range attractive force in practically all realistic potential models for nonpolar molecules. We thought it would be interesting to compare C_6 values obtained from molecular beam scattering experiments with those which could be inferred from the potentials which CCK arrived at from transport and virial properties. Accordingly, we measured total cross sections for the scattering of a hydrogen beam by methane, ethane, propane, and *n*-butane.

The apparatus and procedure are described in detail elsewhere (Nenner et al., 1975). It will suffice here to outline the essential features of the method. Hydrogen at 298°K and 133 kN/m^2 (1 000 torr) is expanded through a sonic orifice 0.1 mm in diameter to form a supersonic free jet in a chamber maintained at 1.33 N/m^2 (10^{-2} torr). A molecular beam is extracted from the core of the jet through a conical brass skimmer into a collimating chamber maintained at 133 μN/m^2 (10^{-6} torr) and then through a collimating slit into a test chamber maintained at about 13 μN/m^2 (10^{-7} torr). In this test chamber the beam molecules pass successively through a second collimating slit, a scattering box, and then into an ionization gauge detector. The detector signal measures the beam intensity I_o when the scattering box is empty and I when there is target gas in the box. The density n_s of target molecules is determined by measurement of box pressure with a capacitance manometer (MKS Baratron 90-M-XR). The attenuation of the beam is described by the Beer's law relation

$$I/I_o = e^{-Qn_sL} \tag{1}$$

where L is the path length over which scattering occurs and Q is the scattering cross section. The angular resolution of our apparatus is high enough [0.77×10^{-3} rad by the Kusch (1964) criterion] and the velocity spread in the beam molecules is narrow enough so that by applying small corrections (von Busch, 1966; Berkling et al., 1962) we could convert our measured Q's into absolute total cross sections Q_t's. Absolute values of the Ar-Ar total cross section determined in our apparatus are within 2% of the best previous experimental values (Rothe and Neynaber, 1965; Swedenburg, 1972). Consequently, we believe that the hydrogen-hydrocarbon values reported here are similarly accurate. It is noteworthy that the apparatus is controlled by a PDP 11/40 minicomputer which provides on line processing of the data. Each reported cross section is in effect the average of forty-eight independent measurements of I, I_o, and n_s. The standard deviation ranges from 0.6 to 1.5%.

From absolute values of Q_t the Van der Waals coefficient C_6 can be obtained by means of the Schiff-Landau-Lifshitz approximation (1956, 1959) which, for our pres-

TABLE 1. VAN DER WAALS COEFFICIENTS FOR HYDROGEN-HYDROCARBON SYSTEMS

Source	Methane	Ethane	Propane	*n*-Butane
Present experiments				
Q_t — total scattering cross section at 2 500 m/s (A^2)	161	230	280	311
Δ — standard deviation (%)	1.3	0.6	0.7	1.5
C_6 — Van der Waals coef. (erg cm^6 × 10^{60})	47.5	116	187	242
CCK—L-J (12-6) potential				
ϵ/k — (K)	66.8	69.2	76.4	75.8
σ — (A)	3.36	3.81	4.12	4.31
C_6 — (erg cm^6 × 10^{60})	53.1	117	206	269
CCK—Exp-6 potential				
ϵ/k — (K)	58.2	60.4	66.7	66.1
σ — (A)	3.48	3.97	4.28	4.47
C_6 — (erg cm^6 × 10^{60})	63.5	143	250	322
Slater-Kirkwood approximation				
α — polarizability (A^3) (For H_2 $\alpha = 0.806$) (Rothe and Helbing, 1969)	2.56	4.39	6.23	8.00
N — Valence electrons	8	14	20	26
C_6 — (erg cm^6 × 10^{60})	43.2	74.5	106	136

ent purpose, can be written as

$$Q_t = 8.083\ (C_6/\hbar g)^{2/5} \tag{2}$$

where $\hbar$ is Planck's constant, and g is the relative velocity of the beam and target molecules, in our case adjusted to 2 500 m/s. C_6 values can also be obtained from the parameters of the optimum potentials deduced for these systems by CCK. In the case of the L-J (6-12) potential, $C_6 = 4\epsilon\sigma^6$. For the Exp-6 potential, $C_6 = 4.426\epsilon\sigma^6$. In these expressions ϵ is the well depth and σ is the separation when the potential energy is zero. It is also possible to calculate C_6 values from the well-known Slater-Kirkwood (1931) approximation

$$C_6 = \frac{25.1 \times 10^{-60}\, \alpha_1\alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}}\ \text{erg cm}^6 \tag{3}$$

where α is the polarizability in A^3 and N is the number of valence electrons. The subscripts relate to the interacting molecular partners.

In Table 1 we have summarized the C_6 values obtained by each of these methods along with appropriate supporting data. The concordance leaves something to be desired. The best agreement is between our values from scattering cross sections and those from the CCK 6-12 potential. The latter are about 15% higher. The worst discrepancy is between our values and those obtained by the Slater-Kirkwood approximation. The hydrogen-methane values agree within 5%, but the discrepancy is almost 70% for propane and butene.

It is not too surprising that there should be discrepancies between C_6 values obtained from total scattering cross sections and those derived from potentials obtained by fitting transport data. In the first place, transport and virial coefficient data are the consequence of averaging over velocity as well as orientation. In the second place, real potentials, especially for polyatomic molecules, are too complex to be faithfully represented over the whole range of internuclear separation by simple two-parameter expressions such as the 12-6 or the Exp-6 potentials. In the third place, and most important when an oversimplified potential is invoked, transport processes and virial behavior are dominated by what happens in relatively energetic collisions at the relatively small internuclear separations of the same order as σ. Scattering experiments to determine total cross sections are by design most sensitive to what happens during encounters at very large internuclear separations, way out on the attractive part of the potential. That is why total cross sections are a good source of information on C_6. That these differences are important is emphasized by the results summarized here. The Exp-6 potential fits the transport and virial data better than the 12-6 potential. The C_6 value from the 12-6 potential is much closer to the value from the total scattering cross section.

More disappointing is the large discrepancy between the C_6 values from either scattering cross sections or transport data and the values from the Slater-Kirkwood approximation. The discrepancy cannot simply be dismissed as being due to the complexity of the target molecules. There is little doubt that the long range attraction is indeed due to the induced dipole-induced dipole interaction which Slater-Kirkwood accounts for in terms of polarizabilities. We used experimental polarizabilities in applying the approximation. Moreover, in the experiments with argon mentioned earlier, we have used as scattering centers some thirty aliphatic hydrocarbons up to and including molecules as complex as octane. The values of C_6 obtained in those experiments generally agreed with the Slater-Kirkwood estimates to within less than 10%. It is not immediately apparent why there should be much poorer agreement in the results reported here. It may be due to the relatively high velocity of hydrogen molecules which results in relatively small internuclear separations for detectable scattering. We are pursuing the implications of this idea. Meanwhile, we are presently persuaded that for relatively large and slow molecules, Slater-Kirkwood approximations are probably at least as reliable for the determination of C_6 values as are simple potentials inferred from transport data. For encounters between small fast molecules and large slow ones, the Slater-Kirkwood approximation is suspect.

ACKNOWLEDGMENT

This work was supported by the Air Force Office of Scientific Research under Grant AFOSR-72-2236 D.

LITERATURE CITED

Berkling, K., R. Helbing, K. Kramer, H. Pauly, Charles Schlier, and P. Toschek, "Effektive Stossquerschnitte bei Streuversuchen," *Zeit. Phys.*, **166,** 406 (1962).

Chu, T. C., P. S. Chappelear, and Riki Kobayashi, "Unlike Pair-Potential Interaction Constants for Hydrogen-Light Hydrocarbon Systems," *AIChE J.*, **21,** 173 (1975).

Kusch, P., "Notes on Resolution in Scattering Measurements," *J. Chem. Phys.* **40,** 1 (1964).

Landau, L. D., and E. M. Lifshitz, *Quantum Mechanics*, Pergamon Press, New York (1959).

Nenner, T., H. Tien, and J. B. Fenn, "Total Cross Section Measurements for the Scattering of Argon by Aliphatic Hydrocarbons," *J. Chem. Phys.*, **63,** 5439 (1975).

Rothe, E. W., and R. H. Neynaber, "Measurements of Absolute Total Cross Section," *ibid.*, **43,** 4177 (1965).

Rothe, E. W., and R. K. B. Helbing, "Glory Scattering of Lithium by a Series of Molecules, II Fluorocarbons and Hydrocarbons," *ibid.*, **50,** 3531 (1969).

Schiff, L. I., "Approximation Method for High-Energy Potential Scattering," *Phys. Rev.*, **103,** 443 (1956).

Slater, J., and J. G. Kirkwood, "The Van der Waals Forces in Gases," *ibid.*, **37,** 682 (1931).

Swedenburg, R. L., "Total Elastic Scattering Cross Sections for the Rare Gases at Thermal Energies," Ph.D. dissertation, Univ. Va., Richmond, Va. (1972).

von Busch, F., "Der Einfluss des Winkelauflosungsvermogens auf die Messung totaler atomarer Streuquerschnitte," *Zeit. Phys.*, **193,** 412 (1966).

Manuscript received July 14, 1975; revision received September 23, and accepted September 29, 1975.

Transport Through a Growing Boundary Layer to a Permeable Wall

M. H. FRIEDMAN

Applied Physics Laboratory
The Johns Hopkins University
Laurel, Maryland 20810

Boundary layer techniques are commonly used to describe the transport of heat or mass[*] in flowing systems. For fully developed steady flow through a pipe of uniform cross section, the shear rate at the pipe wall is uniform and constant (U/C), and boundary layer solutions are available [for example, Bird et al., (1960)] for wall flux when the U/C concentration at the wall is specified and for wall concentration when the U/C wall flux is given. Steady state solutions are also available for these boundary conditions of the first and second kind for the cases in which nonuniform concentration or flux profiles are specified, or when wall shear varies spatially (Lighthill, 1950; Chambre and Acrivos, 1956; Acrivos and Chambre, 1957; Friedman and Ehrlich, 1975; Ehrlich and Friedman, 1976).

If the flow is past a surface which is permeable to the solute, then the interface boundary condition is more complex and the variation along the wall of interfacial concentration or flux must in general be found by iterative numerical techniques (Friedman and Ehrlich, 1975; Ehrlich and Friedman, 1976). For the case of U/C shear and a radiation boundary condition (Carslaw and Jaeger, 1959), an explicit solution for C_w and g can be found; the purpose of this note is to present and discuss it.

ANALYSIS

It is easiest to begin with Lighthill's (1950) Equation (26), which relates the Laplace transforms of heat flux and wall temperature under a thermal boundary layer in a longitudinally varying shear field. Translated into mass transfer variables, his equation is

$$2^{1/2} L \left\{ \frac{\overline{G}(t)}{\overline{S}^{1/2}(t)} \right\} = -\alpha p^{1/3} L \{\chi(t)\} \qquad (1)$$

where $\overline{G}$, $\overline{S}$, and χ are defined on the independent variable

$$t = \frac{2^{1/2}}{Pe'} \int_0^{\overline{x}} \Omega_w{}^{1/2} (\overline{x}') d\overline{x}', \; \alpha = (2/3)^{2/3}\Gamma(2/3)/\Gamma(4/3),$$

and p is the Laplace variable. In deriving Equation (1), the nondimensional concentrations in the free stream and upstream of the concentration boundary layer ($\overline{x} < 0$) were set at zero.

In dimensional terms, the boundary condition for radiation into a medium at zero concentration (Carslaw and Jaeger, 1959) at the wall is $g = kC_w$. In nondimensional terms, $\overline{G}(t) = Sh \cdot \chi_1(t)$. Note that the upstream value of χ is zero, while that of χ_1 is unity ($C_w = C_o$); thus, for this problem, where the governing differential equation is linear in the derivatives of concentration, $\chi_1 = 1 + \chi$. When the nondimensional wall shear is uniformly Ω_w and the transforms of $\overline{G}(t)$ and $\chi(t)$ in Equation (1) are replaced by those of the corresponding functions of $\chi_1(t)$, one finds

$$L\{\chi_1(t)\} = \frac{1}{cp^{2/3} + p}$$

where $c = 2^{1/2} \cdot Sh/(\Omega_w{}^{1/2}\alpha)$.

The transform has a branch point at the origin. The inversion theorem is employed to find $\chi_1(t)$ by using a branch cut along the negative real axis:

$$\chi_1(t) = \frac{3^{1/2}c}{2\pi} \int_0^\infty \frac{\exp(-tx')}{(x')^{4/3} + cx' + c^2(x')^{2/3}} \, dx'$$

For the uniform shear case considered here, the independent variable t can be replaced by $(2\Omega_w)^{1/2}\overline{x}/Pe'$. By replacing the dummy variable x' by c^3z^3, where z is a new dummy variable, the reduced interfacial concentration defined on $\overline{x}$ is given by

$$\overline{C}_w(\overline{x}) = \frac{3^{3/2}}{2\pi} \int_0^\infty \frac{\exp(-b\gamma z^3)}{z^2 + z + 1} \, dz \qquad (2)$$

where $b = [\Gamma(1/3)/\Gamma(2/3)]^3/3 = 2.58$ and $\gamma = Sh^3 \cdot \overline{x}/$

---

[*] This research was initiated to address a problem related to solute transport in arteries and will be phrased in terms of mass transfer variables. The extension to other scalars is trivial.