Van der Waals Constants for Hydrogen and Light Alkane Pair Interactions

GERALD F. THOMAS
and
WILLIAM J. MEATH

Department of Chemistry
University of Western Ontario
London, Ontario, Canada N6A 3K7

Recently, Tien et al. (1976) have reported total cross sections for the scattering of molecular beams of hydrogen molecules by methane, ethane, propane, and *n*-butane and used the results to obtain van der Waals constants C_6, the coefficients of the inverse sixth power term $[-C_6/R^6]$ in the intermolecular separation R which describes the long range attractive force between the nonpolar molecules involved in the scattering experiments. As pointed out by these authors, their C_6 values are very different from those inferred by them from the Lennard-Jones (12-6) or modified Buckingham (Exp-6) potentials, obtained by Chu et al. (1975) from analyses of experimental transport and second virial data, or from the Slater-Kirkwood approximation (Hirschfelder et al., 1954) for C_6.

The purpose of this note is to present results for the van der Waals coefficients, with an estimated error of less than 10%, for all pair interactions arising between hydrogen, methane, ethane, propane, and *n*-butane molecules. The results for the interaction of hydrogen with methane, ethane, propane, and *n*-butane, which are in substantial disagreement with those obtained from either the scattering experiments or from the transport or virial data, are used to help discuss some of the reasons for the lack of agreement between C_6 values determined using various techniques.

The lead term in the orientation averaged R^{-1} expansion of the long range interaction energy between two nonpolar molecules A and B is the London dipole-dipole dispersion energy, $-C_6(A, B)R^{-6}$, where, in erg cm^6,

$$C_6(A, B) = (9.5736 \times 10^{-61}) \frac{3}{2} \sum_{i,j} \frac{f_i(A) f_j(B)}{E_i(A) E_j(B) (E_i(A) + E_j(B))} \quad (1)$$

Here, $f_i(A)$ and $E_i(A)$ are the dipole oscillator strength and excitation energy, in atomic units, associated with the transition from the ground state to the i^{th} excited state of molecule A (Dalgarno et al., 1967). The sums in (1) represent sums and integrals, respectively, over the discrete and continuum dipole allowed transitions of molecules A and B. The energy $-C_6(A, B)R^{-6}$ is an accurate representation of the orientation averaged interaction energy only for intermolecular distances sufficiently large that electron exchange and charge overlap effects between the two interacting molecules are negligible (Longuet-Higgins, 1956; Dalgarno, 1963; Dalgarno and Davison, 1966; Kreek et al., 1970, and references therein). It is the coefficient defined by (1) that yields the dipole-dipole dispersion energy, and it is this coefficient that is represented by the Slater-Kirkwood approximation.

At the present time, accurate values of the dipole-dipole dispersion energy, for molecules of the size of interest here, can only be obtained from (1) if the dipole oscillator strength distributions (DOSDs) for the interacting molecules are known over a wide range of excitation energies (Dalgarno et al., 1967; Zeiss and Meath, 1977; Thomas and Meath, 1977). The construction of reliable DOSDs for this purpose is a difficult task and depends on the availability of a great deal of theoretical and experimental data. On the other hand, Dalgarno and co-workers (1967) have given a simple procedure for determining effective DOSDs for atoms and molecules from which C_6 values can be reliably estimated. The method involves minimization of the function

$$F(g_1, \tilde{\omega}_1, g_2, \tilde{\omega}_2) = \sum_{i=1}^{M} \left\{ [n(\omega_i) - 1] - \left(\frac{g_1}{\tilde{\omega}_1^2 - \omega_i^2} + \frac{g_2}{\tilde{\omega}_2^2 - \omega_i^2} \right) \right\}^2 \quad (2)$$

with respect to the parameters g_1, $\tilde{\omega}_1$, g_2, and $\tilde{\omega}_2$, where the $n(\omega_i)$, $i = 1, 2, \ldots, M$, are M refractive index data points measured at photon energies ω_i for a gas made up of the relevant molecules. This procedure yields effective oscillator strength-excitation energy pairs, namely, $(g_1, \tilde{\omega}_1)$

0001-1541-79-1889-0352-$00.75.

and (g_2, $\tilde{\omega}_2$), which give the following approximation (Dalgarno et al., 1967) for C_6:

$$\tilde{C}_6(A, B) = (9.5736 \times 10^{-61}) \frac{3}{2} \sum_{i,j=1}^{2} \frac{g_i(A) g_j(B)}{\tilde{\omega}_i(A)\tilde{\omega}_j(B)(\tilde{\omega}_i(A) + \tilde{\omega}_j(B))} \quad (3)$$

The effective oscillator strengths obtained by fitting (2) underestimate the Thomas-Reiche-Kuhn (Hirschfelder et al., 1954) sum rule $\sum_i f_i(A) = N_A$, where N_A is the number of electrons in A, which leads to results for $\tilde{C}_6(A, B)$ which are lower than those obtained by more refined techniques (when available). The recommended values of $\tilde{C}_6(A, B)$ are obtained by scaling $\tilde{C}_6(A, B)$ upward by about 5% and should be accurate to within 5 to 10% if the refractive index data on which they are based are reliable (Dalgarno et al., 1967).

Using results for g_1, g_2, $\tilde{\omega}_1$, and $\tilde{\omega}_2$ obtained from the analyses of refractivity data for hydrogen, methane, ethane, and propane by Landolt-Börnstein (1962), we have evaluated $\tilde{C}_6(A, B)$ for these molecules using (3). Recommended values for $C_6(A, B)$ are obtained from these results by a maximum upward scaling of about 5% based on accurate results for the dipole-dipole dispersion energy constants for the hydrogen-hydrogen, hydrogen-methane, and methane-methane interactions (Thomas and Meath, 1977; Margoliash and Meath, 1978) and depending upon the degree to which the Thomas-Reiche-Kuhn sum rule is fulfilled. For the evaluation of results involving n-butane we have minimized (2) using the refractivity data of Watson and Ramaswamy (1936); the optimized parameters for n-butane are $g_1 = 7.1538$, $\tilde{\omega}_1 = 0.4454$, $g_2 = 24.7535$, $\tilde{\omega}_2 = 1.3548$. The resulting values for $\tilde{C}_6(A, n\text{-butane})$ are then scaled upward by up to 15% to obtain the recommended values. The scaling was based on a comparison of the $C_6(A, B)$ values obtained for methane, ethane, and propane based on Watson and Ramaswamy (1936) refractivity data with those obtained using Landolt-Börnstein data. A larger upward scaling is required when Watson and Ramaswamy data are used, since they are available only for a relatively narrow wavelength region.

The recommended results for the dipole-dipole dispersion energy coefficients are summarized in Table 1 which also contains the results for $C_6(H_2, B)$ obtained by Tien et al. (1976). The recommended results are all much smaller than those obtained in the scattering work, with the disagreement increasing markedly as B increases in size; the disagreement is 25, 70, 90, and 100% for B = methane, ethane, propane, and n-butane, respectively. Further, the values obtained by using the Slater-Kirkwood approximation for C_6, which were used in Tien et al. (1976) for comparison purposes, are higher* by from 9 to 17% than our recommended values. The C_6 values obtained from the analyses of transport and virial data (Chu et al., 1975; see the table in Tien et al., 1976), which depend on the approximate potential energy function used to interpret the data, are generally considerably higher than those obtained from the scattering data.

Table 1. Recommended Values for the Dipole-Dipole Dispersion Energy Coefficients $C_6(A, B)$, in Units of 10^{-60} erg cm^6, for all Pair Interactions Taken from Ground State Hydrogen, Methane, Ethane, Propane, and n-butane. The Probable Errors in These Results Should Not Exceed 10%, and the Results for C_6(Hydrogen, Hydrogen), C_6(Hydrogen, Methane), and C_6(Methane, Methane) are in Agreement with Known Accurate Results by Construction. The C_6 Values Recently Obtained by Tien et al. (1976), Indicated by a † in the Table, are Included for Comparative Purposes

$C_6(A, B)$	H_2	CH_4	C_2H_6	C_3H_8	nC_4H_{10}
H_2	11.6	37.9	67.0	98.3	117
CH_4	47.5†	124	220	322	380
C_2H_6	116†		389	572	674
C_3H_8	187†			846	993
nC_4H_{10}	242†				1 171

The reasons for the lack of agreement between C_6 values obtained from the total scattering cross-section measurements and those derived from fitting transport and virial data have been adequately discussed by Tien et al. (1976). The point to be emphasized here is that analogous arguments (Dalgarno, 1963; Dalgarno and Davison, 1966) apply with respect to disagreements between the C_6 values obtained from scattering, transport, or virial data and those obtained from the defining Equation (1) by using either DOSD or refractivity data or from the Slater-Kirkwood approximation. Detailed studies have shown that the latter yields results that are usually high by up to about 20% when compared to reliable C_6 values (Kramer and Herschbach, 1970; Zeiss and Meath, 1977). In particular, results obtained from scattering experiments can be considerably greater than the recommended C_6 values unless the beam experiments are such that only the very long range part of the potential energy curve for the interacting molecules is being examined. If this is not the case, then the C_6 values obtained by analyzing the total cross sections by using a potential energy represented by $-C_6R^{-6}$ are not the dipole-dipole dispersion energy coefficients. Rather, $-C_6R^{-6}$ effectively represents the total attractive part of the potential, and the parameter C_6 contains contributions from higher-order dispersion and induction energies [including Keesom alignment energies (Hirschfelder et al., 1954) for the interaction of molecules having permanent moments] and their charge overlap and electron-exchange correction terms.

As suggested by Tien et al. (1976), the reason for the discrepancies between the scattering results for $C_6(H_2, B)$ and our recommended results (and the Slater-Kirkwood approximations to them) may well be largely due to the high velocity of the hydrogen molecules used in the experiments. This is further supported by the fact that $C_6(Ar, B)$ values we have obtained using $C_6(Ar, Ar) = 64.33 \times 10^{-60}$ erg cm^6 (Tang et al., 1976), our recommended values for $C_6(B, B)$, values for the relevant dipole polarizabilities (Maryott and Buckley, 1953), and the Moelwyn-Hughes (1964) combination rule, namely $C_6(Ar, B) = 88.8$, 168, 233, and 272 for B = methane, ethane, propane, and n-butane are in reasonable agreement with results obtained from the Slater-Kirkwood approximation and from total scattering cross sections for the scattering of argon beams by methane, ethane, propane, and n-butane by Nenner, Tien, and Fenn (1975). The relative velocity of the argon atoms is about a factor of 5 smaller than for the hydrogen molecules in the two beam experiments with the result that relatively small intermolecular separations are sampled in the experiments involv-

* In the Slater-Kirkwood formula even the usual choice of N, as the number of valence electrons, usually leads to overestimates of C_6 since, like transitions involving inner shell electrons, not all excitations involving valence electrons contribute significantly to the oscillator strength sums occurring in (1).

ing hydrogen (Tien et al., 1976; Nenner et al., 1975). Studies of the validity of the Moelwyn-Hughes combination rule indicate it yields results for $C_6(A, B)$ that are reliable to within 2% if the input data are accurate (Kramer and Herschbach, 1970; Zeiss and Meath, 1977; Margoliash and Meath, 1978). Other discussions of problems associated with obtaining long range interaction coefficients from beam scattering experiments can be found in the articles by Bernstein (1966), Bernstein and Muckerman (1967), and Bernstein and La Budde (1973). Also implicit in this discussion is the usual assumption that the scattering is dominated by the orientation average of the intermolecular potential (isotropic part of the potential). The importance of anisotropic intermolecular forces in beam scattering experiments, and their proper incorporation into the theoretical analysis of the problem, is of considerable interest and importance (see, for example, Bickes et al., 1975, and references therein). The effects of anisotropic forces need not be negligible even for interactions involving essentially nonpolar molecules if the relative velocity of the collision partners is high and if one (or both) of the molecules is elongated.

Finally, it should be stressed, relative to suggestions made by Tien et al. (1976), that, as in the case of the rigorously defined dipole-dipole dispersion energy (1), the validity of the Slater-Kirkwood approximation does not depend on the conditions under which a particular experiment, which is used to determine C_6, is carried out. Rather, the quality of the results obtained for C_6, as a representation of the true dipole-dipole dispersion energy coefficient, depends on the nature of the potential form used to fit the experimental data and on what part of the potential is responsible for the experimental observable. If reasonably accurate C_6 values are known, it is often useful to use these results to help specify the long range part of the potential energy curve and to use adjustable parameters to fit other less well-known portions of the potential (Smith et al., 1977; Barker et al., 1970, 1974, and references therein).

ACKNOWLEDGMENT

This research was supported by a grant from the National Research Council of Canada.

NOTATION

$C_6(A, B)$ = London dipole-dipole dispersion energy constant for the interaction between molecules A and B.

R = intermolecular separation

$-C_6(A, B)R^{-6}$ = London dipole-dipole dispersion energy

$[f_i(A), E_i(A)]$ = dipole oscillator strength—excitation energy pair for molecule A corresponding to the transition from the ground state to the i^{th} excited state

$n(\omega_i)$ = refractive index of a gas for photon energy ω_i

$[g_i(A), \tilde{\omega}_i(A)]$ = effective dipole oscillator strength—excitation energy pair

$\tilde{C}_6(A, B)$ = approximation to $C_6(A, B)$

N_A = number of electrons in molecule A

LITERATURE CITED

Barker, J. A., R. A. Fisher, and R. O. Watts, "Liquid Argon: Monte Carlo and Molecular Dynamics Calculations," *Molec. Phys.*, **21**, 657 (1970).

Barker, J. A., R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, "Interatomic Potentials for Krypton and Xenon," *J. Chem. Phys.*, **61**, 3081 (1974).

Bernstein, R. B., "Quantum Effects in Elastic Molecular Scattering," *Advan. Chem. Phys.*, **10**, 75 (1966).

———, and J. T. Muckerman, "Determination of Intermolecular Forces via Low-Energy Molecular Beam Scattering," *ibid.*, **12**, 389 (1967).

Bernstein, R. B., and R. A. La Budde, "On the Analysis of Glory Scattering Data for the Extraction of Information on the Interatomic Potential Well," *J. Chem. Phys.*, **58**, 1109 (1973).

Bickes, R. W., Jr., G. Duquette, C. J. N. van den Meijdenberg, A. M. Rulis, G. Scoles, and K. M. Smith, "Molecular Beam Scattering Experiments with Polar Molecules: Measurement of Differential Collision Cross Sections for H_2O + H_2, He, Ne, Ar, H_2O and NH_3 + H_2, He, NH_3," *J. Phys. B.*, **8**, 3034 (1975).

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

Dalgarno, A., "Intermolecular Forces," *Rev. Mod. Phys.*, **35**, 611 (1963).

———, and W. D. Davison, "The Calculation of van der Waals Interactions," *Advan. At. Mol. Phys.*, **2**, 1 (1966).

Dalgarno, A., I. H. Morrison, and R. M. Pengelly, "Long-Range Interactions Between Atoms and Molecules," *Int. J. Quant. Chem.*, **1**, 161 (1967).

Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).

Hirschfelder, J. O., W. Byers Brown, and S. T. Epstein, "Recent Developments in Perturbation Theory," *Advan. Quant. Chem.*, **1**, 255 (1964).

Kramer, H. L., and D. R. Hershbach, "Combination Rules for van der Waals Force Constants," *J. Chem. Phys.*, **53**, 2792 (1970).

Kreek, H., Y. H. Pan, and W. J. Meath, "Charge Overlap Effects. Dependence on the Nature of the Interaction," *Molec. Phys.*, **19**, 513 (1970).

Landolt-Börnstein, "Zahlenwert und Funkionen," 6 Aufl., Bd. II, 8 Teil, 286 Gase und Dümpfe, Springer-Verlag (1962).

Longuet-Higgins, H. C., "The Electronic States of Composite Systems," *Proc. Royal. Soc (London)*, **A235**, 537 (1956).

Margoliash, D. J., and W. J. Meath, "Pseudo Spectral Dipole Oscillator Strength Distributions and Some Related Two Body Interaction Coefficients for H, He, Li, N, O, H_2, N_2, O_2, NO, N_2O, H_2O, NH_3, and CH_4," *J. Chem. Phys.*, **68**, 1426 (1978).

Maryott, A. A., and F. Buckley, "Tables of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," *N.B.S. Circular 537*, U.S. Dept. of Commerce, Washington, D.C. (1953).

Moelwyn-Hughes, E. A., *Physical Chemistry*, 2 ed., Pergamon, New York (1964).

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).

Smith, K. M., A. M. Rulis, G. Scoles, R. A. Aziz, and V. Nain, "Intermolecular Forces in Mixtures of Helium with the Heavier Noble Gases," *ibid.*, **67**, 152 (1977).

Tang, K. T., J. M. Norbeck, and P. R. Certain, "Upper and Lower Bounds of Two- and Three-Body Dipole, Quadrupole, and Octupole van der Waals Coefficients for Hydrogen, Noble Gas, and Alkali Atom Interactions," **64**, 3063 (1976).

Thomas, G. F., and W. J. Meath, "Dipole Spectrum, Sums and Properties of Ground-State Methane and their Relation to the Molar Refractivity and Dispersion Energy Constant," *Molec. Phys.*, **34**, 113 (1977).

Tien, H., T. Nenner, and J. B. Fenn, "Long Range Attractive Forces for Hydrogen-Light Hydrocarbon Pairs," *AIChE J.*, **22**, 405 (1976).

Watson, H. E., and K. L. Ramaswamy, "The Refractive Index Dispersion and Polarization of Gases," *Proc. Royal Soc. (London)*, **A156**, 144 (1936).

Zeiss, G. D., and W. J. Meath, "Dispersion Energy Constants $C_6(A, B)$, Dipole Oscillator Strength Sums and Refractivities for Li, N, O, H_2, N_2, O_2, NH_3, H_2O, NO and N_2O," *Molec. Phys.*, **33**, 1155 (1977).

Manuscript received May 10, 1978; revision received August 2, and accepted August 25, 1978.