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Citation: The Journal of Chemical Physics 55, 4012 (1971); doi: 10.1063/1.1676694

View online: http://dx.doi.org/10.1063/1.1676694

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A Shorter Method of Calculating LennardJones (12–6) Potential Parameters from Gas Viscosity Data
Estimation of Lennard-Jones (6,12) Pair Potential Parameters from Gas Solubility Data

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(Received 27 May 1971)

The Lennard-Jones (6,12) pair potential parameters for solvents can be calculated from gas solubility data by using the scaled particle theory to calculate the work of cavity formation. Values of the hard sphere diameter \( \sigma_1 \) and the energy parameter \( \epsilon_1/k \) at 298.15 K and 1 atm pressure are reported for 39 liquids, polar as well as nonpolar. These parameters are discussed in relation to values determined by other methods.

INTRODUCTION

In a series of papers,1-3 the authors have used gas solubility data for the determination of Lennard-Jones (6,12) pair potential parameters of several organic solvents. This approach, first proposed by Pierotti,4 yielded results which were in excellent agreement1,3 with values reported in the literature, thus lending confidence to the method. In view of the limited number of experimental results5 for compounds normally liquid at 298.15 K and atmospheric pressure, and the fact that all those data were obtained from gas phase studies, the possibility of extracting pair potential parameters for the liquid state from gas solubility data is especially important.

THEORY

The mathematical formalism has been described in detail,3,4 and we therefore just summarize the pertinent equations. The process of dissolving a gas in a liquid is considered to consist of two steps: (a) creation of a cavity, in the liquid, large enough to accommodate a gas molecule and (b) introduction of a gas molecule into the cavity with subsequent interaction with the surrounding solvent. For this anticipated two-step mechanism it can be shown that for very dilute solutions6

\[
RT \ln K_H = G_c + G_i + RT \ln \left( \frac{RT}{V_1} \right).
\]

Here, \( K_H \) is the Henry's law constant defined as \( K_H = P/\rho \), where \( P \) is the partial pressure of the gas and \( \rho \) is the density of dissolved gas in the solvent. \( G_c \) and \( G_i \) are the partial molar Gibbs free energy of cavity formation and interaction, respectively, and correspond to steps (a) and (b) above. The molar volume of the solvent is \( V_1 \), \( R \) is the gas constant, and \( T \) is the absolute temperature. The last term in Eq. (1) merely accounts for the change in standard states.

Reiss et al.7 related \( G_c \) to parameters of the solute and the solvent, obtaining

\[
G_c = RT \left[ \frac{y}{1-y} \left( \frac{a_{12}}{a_1} \right)^2 \frac{a_{12}}{a_1} \right] + 18 \left( \frac{y}{1-y} \right)^2 \left( \frac{a_{12}}{a_1} \right)^2 \left( \frac{a_{12}}{a_1} + \frac{1}{2} \right) - \ln(1-y),
\]

where \( y = \pi a_1^2 \rho / 6 \) is the ratio of the hard sphere volume to the molar volume of the solvent, for which we propose the term "compactness factor." The number density is defined by \( \rho = N/V_1 \); \( a_1 \) is the hard sphere diameter of the solvent, and \( N \) is Avogadro's number. The diameter of the cavity to be created is \( a_2 \), and \( a_{12} = (a_1 + a_2)/2 \) is the radius of the sphere which excludes the centers of surrounding solvent molecules.

To express dispersion and repulsive interactions we will use the Lennard-Jones (6,12) pairwise additive potential \( u(r) \) in the form (pure substance)

\[
u(r) = 4\epsilon \left( \frac{(\sigma/r)^{12} - (\sigma/r)^{6}}{\epsilon} \right),
\]

where \( -\epsilon \) is the minimum potential energy and \( \sigma \) is the distance where \( u = 0 \), i.e., the hard sphere diameter. Thus for a system composed of a nonpolar solvent and a nonpolar gas, we obtain1,4,6

\[
\bar{G}_i = -3.555 \pi \rho \sigma \xi^3 (\epsilon_{12}/k),
\]

whereas for a system consisting of a polar solvent (with dipole moment \( \mu_1 \)) and a nonpolar gas (with polarizability \( \alpha_2 \)), an appropriate induced dipole term6 has to be added, viz.,

\[
\bar{G}_i = -3.555 \pi \rho \sigma \xi^3 (\epsilon_{12}/k) - 1.333 \pi \rho N (\mu_1^2 \alpha_2 / \sigma_{12}^3).
\]

As usual, properties with subscripts 1 and 2 refer to the solvent and solute, respectively. The doubly subscripted parameters were derived via the combining rules \( \sigma_{12} = (\sigma_1 + \sigma_2)/2 \) and \( \epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \). Since the potential energy rises very rapidly with decreasing distance, the values of \( \sigma_1 \) and \( \sigma_2 \) are also effectively the values of \( a_1 \) and \( a_2 \).

COMPUTATIONAL PROCEDURES

To carry out our calculations it was necessary to extract the logarithm of the Henry's law constant \( \ln K_H \) at 298.15 K from literature data on gas solubility. This was done by converting the literature data, whenever necessary, to mole fraction solubilities at the reported temperature and 1 atm partial gas pressure, followed by a linear least squares analysis of the form \( RT \ln x_2 = A + BT \). In a few cases, where data of exceptional accuracy were available over a greater temperature interval, they were approximated by a quadratic expression, viz., \( RT \ln x_2 = A + BT + CT^2 \). In both cases, \( x_2 \) at 298.15 K and \( P_2 = 1 \) atm was calculated, yielding the Henry's law constant \( \ln K_H = \ln (P_2/x_2) = -\ln x_2 \).

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A full account of the results of our literature survey is in preparation.

**Evaluation of the Hard Sphere Diameter**

A plot of \( \ln K_H \) vs \( \alpha_2 \), the polarizability of the solutes, gives in general a smooth curve\(^9\) for the rare gases in a particular solvent. Figure 1 shows such a graph for isoctane at 298.15°K and 1 atm partial gas pressure. Similar results are obtained for all solvents considered here. The extrapolation of such a curve to \( \alpha_2 = 0 \) yields a finite value, \( \ln K_{H,0} \). In Ref. 4 it was shown that this procedure is equivalent to obtaining the solubility, expressed as the Henry's law constant, of a hard sphere of diameter \( \sigma = 2.58 \times 10^{-8} \) cm in a specific solvent. This can be formulated as

\[
RT \lim_{\alpha_2 \to 0} \left( \ln K_H \right) = RT \ln K_{H,0} + \frac{\tilde{G}_C + RT \ln \left( \frac{RT}{V_1} \right)}{\alpha_2^2 + 2.58 \times 10^{-8}}.
\]

Insertion of the graphically determined value of \( \ln K_{H,0} \), of \( \tilde{G}_C \) [cf. Eq. (2)] and of the appropriate value for \( V_1 \) into Eq. (6), and the setting of \( \alpha_2 = \alpha_1 = 2.58 \times 10^{-8} \) cm yield an equation for \( \alpha_1 = \sigma_1 \), which can be solved by standard techniques.

The accuracy of the method is limited mainly by (a) uncertainties connected with the extrapolation of the graph \( \ln K_H \) vs \( \alpha_2 \) to \( \alpha_2 = 0 \), and (b) uncertainties in the reported experimental solubilities. The latter point is of special importance for He and Ne because they have a strong influence on the shape of the last portion of the curve and therefore the intercept. Unfortunately, experimental errors with these two gases are generally especially large. We estimate the maximum possible error due to (a) to be of the order of \( \pm 0.03 \times 10^{-8} \) cm. The possible uncertainty stemming from (b) is more difficult to assess because it involves judging the reliability of experimental data. However, in general it should not exceed \( \pm 0.03 \times 10^{-8} \) cm, either.

**Evaluation of the Energy Parameter** \( \epsilon_1/k \)

Rearrangement of Eq. (4) or (5), respectively, leads to

\[
RT \ln K_H - \tilde{G}_C - RT \ln \left( \frac{RT}{V_1} \right) = -3.555 \pi \rho R \sigma_2 \frac{\epsilon_1^{1/2}}{k} \left( \frac{\epsilon_1}{k} \right)^{1/2}
\]

or\(^10\) to

\[
RT \ln K_H - \tilde{G}_C - RT \ln \left( \frac{RT}{V_1} \right) + 1.333 \pi \rho N \frac{\mu_1^2 \alpha_1}{\sigma_1^2} \frac{\epsilon_1}{k} = -3.555 \pi \rho R \sigma_2 \frac{\epsilon_1^{1/2}}{k} \left( \frac{\epsilon_1}{k} \right)^{1/2}.
\]

The left-hand side (lhs) of Eq. (7) or (8) can be calculated from known parameters (including \( \sigma_1 \), determined by the method described above) and results of gas solubility measurements, whereas on the rhs only \( \epsilon_1/k \) remains unknown. Thus, a plot of the lhs vs \( (\epsilon_1/k)^{1/2} \) should give a straight line with slope \( -3.555 \pi \rho R \sigma_2 \epsilon_1^{1/2} \). Figure 2 shows such a graph for isoctane. The necessary properties and parameters for the solutes are listed in Table 1. The molar volumes of the solvents are listed in Table II. Solvent dipole moments were taken from the literature.\(^{11}\)

In determining the energy parameter, we did not use all available experimental data. The exceptions are the following. (a) No results for \( \text{CO}_2 \) in aromatic solvents or solvents containing OH groups were used. In addition, CO\(_2\) data were omitted for acetone and dimethyl sulfoxide since the solubility of carbon dioxide in these solvents shows pronounced anomalies. (b) No results of the solubility of CO in polar solvents were included because of dipole–dipole interaction. (c) The theoretical relations are valid only for very dilute solutions, giving
and the energy parameter $\epsilon/k$, it also contains the compactness factor $y$. Table III compares pair potentials of six solvents obtained from various sources. As one can see, the agreement of our results with data on the gases at 298.15°K: hard sphere diameter $d$, energy parameters obtained by the method outlined above. First, the value of $\alpha_1$. Consequently, the possible over-all uncertainty is relatively poor results for high concentrations (see Ref. 1). We therefore arbitrarily chose $x=0.04$ as an upper limit, considering no solubilities greater than this value.

It is difficult to assess the reliability limits of the energy parameters obtained by the method outlined above. First, the value of $\epsilon/k$ depends somewhat on the number and the kind of gases used for its evaluation. This implies that parameters derived from data for four to six gases are less reliable than parameters deduced from data for 12–14 gases. This is especially true if only rare gas data are available, because of the well known deviation of He and Ne from the linear relationships of Eq. (7) or (8) (cf. Ref. 3). Second, experimental errors in reported solubilities enter directly, and, third, any error in $\sigma_1$ results in a corresponding error in $\epsilon/k$. Consequently, the possible over-all uncertainty is larger than the one connected with the distance parameter, the greatest contribution stemming from the first point mentioned above. Therefore, the values for $\epsilon/k$ for solvents where data for only three gases were available have to be regarded as being very tentative and were placed in parentheses in Table II. For other liquids, we estimate the reliability limit—depending on the number of gases—to be as great as ±15%.

**RESULTS AND DISCUSSION**

Table II gives the results for 39 solvents at 298.15°K and 1 atm. In addition to the distance parameter $\sigma_1$ and the energy parameter $\epsilon/k$, it also contains the compactness factor $y$. Table III compares pair potentials of six solvents obtained from various sources. As one can see, the agreement of our results with data on the gases at 298.15°K: hard sphere diameter $d$, energy parameters obtained by the method outlined above. First, the value of $\alpha_1$. Consequently, the possible over-all uncertainty is relatively poor results for high concentrations (see Ref. 1). We therefore arbitrarily chose $x=0.04$ as an upper limit, considering no solubilities greater than this value.

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obtained through the application of various theories to the measured properties of liquids (Columns b–f) is generally quite satisfactory. Additional comparisons (see Fig. 3) and a detailed discussion follow.

### n-Alkanes and Branched Alkanes

Values for the Lennard-Jones parameters of several \( n \)-alkanes are graphed in Fig. 3. Our results for the hard sphere diameters generally are substantially lower than the ones reported in Ref. 5 (except for \( n \)-hexane), but are in excellent accord with the parameters reported by Nelson and de Ligny\(^7\) and by Salsburg and Kirkwood\(^14\) and with the values derived via the enthalpy of vaporization.\(^1,3\) There is a difference of about \( 0.3 \times 10^{-8} \) cm from the hard sphere diameters calculated by Mayer\(^15\) using experimental surface tensions (Method I) and isothermal compressibilities (Method II) in conjunction with the appropriate expressions from the scaled particle theory\(^7,16\) (below Mayer’s results\(^16\) are referred to as I and II, respectively).

The agreement with respect to \( \varepsilon_1/k \) is less satisfactory. Our figures compare well with the ones of Ref. 14 but are about 100–200°K higher than those of Ref. 13, which in turn are \( \approx 200°K \) higher than the results reported in Ref. 5.

As was pointed out earlier, the \( n \)-alkanes provide an interesting example where the hard sphere diameters from vapor phase studies differ considerably from diameters obtained from properties related to the liquid state. This may be connected with a difference in the degree of colling in the gas and in the liquid state.

As expected, the parameters for the branched alkanes do not differ appreciably from each other. For isooctane, the agreement with results reported by Kobatake and Alder\(^18\) and those derived from the enthalpy of vaporization is quite satisfactory (see Table III). The latter method yields, for 3-methylheptane, \( \varepsilon_1 = 6.52 \times 10^{-8} \) cm; for 2,3-dimethylhexane, \( \varepsilon_1 = 6.50 \times 10^{-8} \) cm; and for 2,4-dimethylhexane, \( \varepsilon_1 = 6.50 \times 10^{-8} \) cm, in good agreement with our values.

### Alicyclic and Aromatic Hydrocarbons

Generally our values agree well with the literature (Table III) with the possible exception of \( \varepsilon_1/k \) of toluene, where only a few other data are available. For \( m \)-xylene, Mayer\(^15\) lists for \( \varepsilon_1 = 5.77 \times 10^{-8} \) cm (I) and \( 5.76 \times 10^{-8} \) cm (II), both \( \approx 0.2 \times 10^{-8} \) cm lower. For methylcyclohexane\(^3\) we obtain from \( \Delta H_v^{298} = 5.98 \times 10^{-8} \) cm, which agrees well with the hard sphere diameter derived from gas solubilities.

### Perfluorinated Compounds

All available literature data are in accord with our findings, as can be seen from Table III, and agree well with results obtained via \( \Delta H_v^{298} \) for perfluoromethylcyclohexane, \( \varepsilon_1 = 6.69 \times 10^{-8} \) cm, and perfluorobenzene, \( \varepsilon_1 = 5.68 \times 10^{-8} \) cm.

### Other Halogen Containing Compounds

Our results for CCl\(_4\) compare quite favorably with others (Table III), as is the case with 1,1,2,2-tetrachloroethane for which Mayer\(^14\) gives for \( \varepsilon_1 = 5.56 \times 10^{-8} \) cm (I) and \( 5.54 \times 10^{-8} \) cm (II). For chlorobenzene \( \varepsilon_1 \) from Ref. 15–5.44 \( \times 10^{-8} \) cm (I) and 5.39 \( \times 10^{-8} \) cm (II) and bromobenzene \( \varepsilon_1 \) from Ref. 15–5.58 \( \times 10^{-8} \) cm (I) and 5.51 \( \times 10^{-8} \) cm (II) we note again a difference of \( \approx 0.2 \times 10^{-8} \) cm.

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**Table III.** Comparison of pair potential parameters from gas solubilities with parameters from other sources at 298.15°K; \( \varepsilon_1 \) in [cm] and \( \varepsilon_1/k \) in [°K].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \varepsilon_1/k )</th>
<th>( \varepsilon_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4-Trisopropylpentane</td>
<td>6.52</td>
<td>6.44</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.63</td>
<td>5.62</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.26</td>
<td>5.25</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.64</td>
<td>5.62</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>5.37</td>
<td>5.39</td>
</tr>
<tr>
<td>Perfluoro-3-heptane</td>
<td>7.04</td>
<td>7.11</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.69</td>
<td>7.02</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.34</td>
<td>7.02</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>5.75</td>
<td>7.02</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.76</td>
<td>4.45</td>
</tr>
</tbody>
</table>

**Note:**
- \( \varepsilon_1/k \) obtained from gas solubilities in the manner described in the text.
- Parameters were taken from Salsburg and Kirkwood\(^6\) who obtained them from the cell theory of liquids.
- Parameters were taken from Kobatake and Alder\(^14\) who obtained them from the liquid state from the equation of state and the vapor pressure.
- \( \varepsilon_1/k \) derived from hard sphere diameters calculated by Mayer\(^15\) and with the values derived via the enthalpy of vaporization.
- From Ref. 15–5.44 \( \times 10^{-8} \) cm (I) and 5.39 \( \times 10^{-8} \) cm (II) we note again a difference of \( \approx 0.2 \times 10^{-8} \) cm.
Alcohols and Acetone

Table III lists Lennard-Jones parameters obtained by the present method and from Refs. 5 and 15. Considering the fact that the alcohols are highly associated in the liquid state, it is somewhat surprising that our results agree so well with the literature ($\epsilon_i/k$ being a little lower than the gas phase values of Ref. 5). However, this is in line with Pierotti's findings for liquid water. For acetone we note satisfactory agreement with regard to the hard sphere diameter, whereas our $\epsilon_i/k$ value is much smaller than the literature value obtained from gas viscosity data. For all compounds, values from Ref. 15 for $\sigma_i$ are again lower by $\approx 0.3 \times 10^{-8}$ cm.

Miscellaneous Compounds

No comparison with other literature data was possible, save for nitrobenzene; Ref. 15 gives for $\sigma_1$ 5.69 $\times 10^{-8}$ cm (I) and 5.59 $\times 10^{-8}$ cm (II), respectively.

Concluding Remarks

From the preceding discussion it is clear that the present method of determining Lennard-Jones (6, 12) pair potential parameters from gas solubility data gives results generally in good agreement with those stems
Density Gradient Measurements of O₂ Dissociation in Shock Waves

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The dissociation of O₂ in mixtures with He, Ar, Kr, and Xe has been studied behind incident shock waves in the temperature range 4000–8500K. Using a laser-beam deflection technique, postshock density gradients were measured on a time scale such that vibrational relaxation and the onset of dissociation are resolvable. The density gradient profiles exhibit a highly characteristic local minimum immediately following the period of vibrational relaxation, at times which correlate well with the induction periods observed by others. The magnitude of the density gradient at this point is interpreted as a measure of the initial dissociation rate, i.e., the rate corresponding to conditions of complete vibrational equilibrium with no dissociation. Rate coefficients thus obtained exhibit a degree of precision unmatched in previous dissociation studies, and agree well in magnitude and temperature dependence with other reported results. Values of k₀₂-M, the rate coefficient for O₂ dissociation due to O₂-M collisions, were determined for M = He, Ar, Kr, and Xe from measurements with mixtures containing 2.5%, 5%, and 10% initial O₂. For O₂-Kr collisions the value

\[ k_{O_2-Kr} = 7.87 \times 10^{14} \exp(-104800/RT) \text{ cm}^3/\text{mole sec}, \]

with R in calories per mole-degree, is obtained, with \( k_{O_2-Xe} \approx 1.6 k_{O_2-Kr} \), \( k_{O_2-Ar} \approx k_{O_2-Kr} \) and \( k_{O_2-Xe} > k_{O_2-Kr} \). The value \( k_{O_2-O_2} \approx 9 k_{O_2-Kr} \), was obtained independently from data for four different inert diluents, supporting the validity of the linear mixture formula for collision partners in O₂ dissociation. The character of the density gradient profiles at later times suggests a higher rate coefficient for collisions with oxygen atoms.

INTRODUCTION

Densitometric measurements have been used extensively to study the rates of vibrational relaxation and dissociation of diatomic molecules in shock waves. In early studies of this type data were extracted from postshock density profiles, determined primarily by interferometric or x-ray absorption measurements. More recently the laser-schlieren technique, which provides a measure of the postshock density gradient with high sensitivity and space/time resolution, has been used successfully to study the vibrational relaxation of numerous gases and gas mixtures. However, to our knowledge no density gradient measurements of diatomic dissociation have been reported heretofore. In this paper we describe such measurements for mixtures of O₂ with various inert gases (He, Ar, Kr, and Xe).

Because of their nonspecific character, densitometric measurements yield unambiguous information about a particular molecular rate process only if this process is effectively decoupled in time from all other processes in the system which produce changes in density. This requirement is met if the rate of the process of interest is very much different from that of any other. For example, rotational relaxation is rapid relative to that of vibration, so that in studies of vibrational relaxation in shock waves rotational degrees of freedom can be assumed to be in continuous equilibrium with the translational temperature. Previous studies in O₂–Ar mixtures have shown that at temperatures up to ~8000K the rate of vibrational relaxation exceeds...