Title
THE VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF FLUIDS VI. RELATIONSHIP OF MOLECULAR PROPERTIES TO THE ACENTRIC FACTOR

Permalink
https://escholarship.org/uc/item/07q451xq

Authors
Danon, F.
Pitzer, Kenneth S.

Publication Date
1961-07-01
THE VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF FLUIDS VI.
RELATIONSHIP OF MOLECULAR PROPERTIES TO THE ACENTRIC FACTOR

F. Danon and Kenneth S. Pitzer
July 1961
THE VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF FLUIDS VI.

RELATIONSHIP OF MOLECULAR PROPERTIES TO THE ACENTRIC FACTOR

by

F. Damon and Kenneth S. Pitzer

Department of Chemistry and Lawrence Radiation Laboratory,
University of California, Berkeley, California

ABSTRACT

The acentric factor, a third parameter in an extended corresponding states treatment of fluids, is related to characteristics of the intermolecular potential. The Kihara core model is considered first and relationships are derived between the acentric factor and the core size for several shapes. The resulting cores for CH₄, CF₄, C(CH₃)₄, C₆H₆ and N₂ are reasonable in view of semi-quantitative theoretical expectations, but the core for CO₂ is somewhat larger than expected. An approximate treatment is given which combines the Kihara core model with an electric quadrupole interaction. The core calculated for CO₂ on this model including the quadrupole moment is of a reasonable size.
A series of recent papers\textsuperscript{1} presents a numerical equation which represents the volumetric and thermodynamic properties of normal fluids in terms of the usual reduced variables of corresponding states together with the acentric factor. Paper III of the series gives an empirical second virial coefficient in these terms.

The satisfactory results obtained in the evaluation of thermodynamic properties of normal fluids by this empirical scheme led us to study further the acentric factor in an attempt to correlate it with molecular properties. The results are given in this paper.

Paper I includes an extensive discussion of the nature of intermolecular forces between the molecules of normal fluids and mentions several mathematical models which may be expected to yield good approximations to these forces in particular cases.\textsuperscript{2}


Most of these proposals are limited in their application to a particular class of normal fluids, such as those with spherical molecules, but the core model of Kihara is quite general in nature. Kihara assumes a core of any shape within each molecule and takes the intermolecular potential to be the Lennard-Jones potential for the shortest distance between the outer surfaces of molecular cores. Thus the potential is

\[
U = U_0 \left[ \left( \frac{\rho}{\rho_0} \right)^{12} - 2 \left( \frac{\rho}{\rho_0} \right)^6 \right]
\]

where \( \rho \) is the shortest distance between cores and \( \rho_0 \) is this distance for the potential minimum.

In paper I Kihara's functions for this model were reduced on the Boyle point basis to equations for the second virial coefficient. Consequently, a comparison of these equations based on the core model with the empirical second virial coefficients of paper III provides a convenient way of relating the acentric factor to this molecular model.

Our results indicate in most cases smaller cores than those assumed by Kihara from molecular structure information and this conclusion finds support in recent independent reports on benzene and methane as well as the general considerations of the intermolecular potential in paper I.

\[3\] T. Kihara, Rev. Mod. Phys. 25 839 (1953) and references given therein.


\[5\] G. Thomas, Nature, 187 229 (1960)
The equation for the second virial coefficients given in III in dimensionless form is

\[
\frac{B}{RT_c} = \frac{B_0}{RT_c} + \omega \frac{B_1}{RT_c}
\]

(2)

where

\[
\frac{B_0}{RT_c} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3}
\]

(2a)

\[
\frac{B_1}{RT_c} = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^3}
\]

(2b)

and

\[
\omega = -\log P_r - 1.000
\]

(2c)

where \(T_r\) is the reduced temperature \(T/T_c\) and \(P_r\) in equation (2c) is the reduced vapor pressure \(P/P_c\) at \(T_r = 0.7\). It is convenient to transform equation (2) from the critical point basis to the Boyle point basis whereupon the result may be compared with equations (15), (15a) and (15b) of paper I. At the Boyle point, \(B = 0\), \(T = T_B\), and we define the Boyle volume

\[
V_B = \left[ T \frac{dV}{dT} \right]_{T = T_B}
\]

(3)

In this special case of zero acentric factor equation (2a) readily yields the result \(T_r = 2.656\) at the Boyle point and \(V_B = 0.1651 RT_c/\rho_c\) (with \(\omega = 0\)). Substitution of these results gives

\[
\frac{B_0}{V_B} = 0.3736 - 0.7512 \left( \frac{T_B}{P_B} \right) - 0.1185 \left( \frac{T_B}{P_B} \right)^2 - 0.0039 \left( \frac{T_B}{P_B} \right)^3
\]

(4)

The values for \(T_B\) and \(V_B\) for \(\omega = 0\) may be substituted into equation (2b), but we find then that the general equation for non-zero values of the acentric factor indicates that \(T_B\) and \(V_B\) depend on \(\omega\) as well as the critical constants. Hence the criterion for the Boyle point must be reapplied to the
The general equation (2) and yields
\[ T_B = \frac{2.656 T_c}{(1 + 1.02 T_0)} \quad \text{and} \quad V_B = \left( \frac{RT_c}{P_c} \right) (0.1651 + 0.1981\lambda) \]

Now the second virial coefficient is

\[ B = B^{(0)} + w B^{(1)} + \cdots \]  \hspace{1cm} (5)

with
\[ \frac{B^{(1)}}{V_B} = -0.6087 + 1.11760 \left( \frac{T_B}{T} \right) - 0.5299 \left( \frac{T_B}{T} \right)^2 - 0.0586 \left( \frac{T_B}{T} \right)^3 \]
\[ - 1.79 \times 10^{-5} \left( \frac{T_B}{T} \right)^5 \]  \hspace{1cm} (6)

The last term in equation (6) is negligible except at low temperature and can usually be omitted. In these transformations only linear terms in \( \omega \) were retained.

We now wish to compare equations (4), (5) and (6) with the corresponding equations for the core model which were expressed in paper I as

\[ \frac{B}{V_B} = \left[ \frac{B}{V_B} \right]_0 + x \left[ \frac{\partial}{\partial x} \left( \frac{B}{V_B} \right) \right]_0 \quad \text{x} = 0 \]  \hspace{1cm} (7)

where \( x \) is a parameter related to the core size. Equations (15a) and (15b) of I give the expressions for the two terms as functions of \( \left( \frac{T_B}{T} \right) \). The first term is just the usual Lennard-Jones function since \( x = 0 \) corresponds to zero core size. The empirical equation for zero acentric factor, i.e. for \( \text{Ar}, \text{Kr}, \text{and Xe} \), is very similar to the Lennard-Jones function but a distinctly better fit is obtained with equation (7) if \( x = 0.24 \). The agreement is then within 0.5\% over the range of validity of the empirical equation.

If the core model is in satisfactory agreement with the experimental data, the second term in equation (7) must equal \( B^{(1)}/V_B \) given by equation (6) for some value of \( x \). Table I gives this comparison for \( x = 7.0\alpha \) and shows good agreement over the range of interest.
## TABLE I

<table>
<thead>
<tr>
<th>$\frac{T_B}{T}$</th>
<th>$\frac{B(1)}{V_B}$</th>
<th>$-7.0 \left[ \frac{g}{E^a(\frac{B}{V_B})} \right]_{z=0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.027</td>
<td>0.026</td>
</tr>
<tr>
<td>1.0</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>1.5</td>
<td>0.169</td>
<td>0.166</td>
</tr>
<tr>
<td>2.0</td>
<td>0.690</td>
<td>0.690</td>
</tr>
<tr>
<td>2.5</td>
<td>1.611</td>
<td>1.625</td>
</tr>
<tr>
<td>3.0</td>
<td>3.010</td>
<td>3.020</td>
</tr>
</tbody>
</table>
This comparison of equations (5) and (7) has resulted in agreement provided

\[ x = 7.0 \omega + 0.24 \]  

(8)

Kihara's general expression for the second virial coefficient is

\[ B = \frac{2\pi}{3} \rho_0^3 P_3(z) + \frac{M_0}{4\pi} \left( s_0 + \frac{M_0^2}{4\pi} \right) \rho_0 F_1(z) + \left( v_0 + \frac{M_0 v_0}{4\pi} \right) \]  

(9)

where \( z = \frac{v_0}{4\pi} \), \( M_0 \) is the surface integral of the mean curvature of the core, \( S_0 \) and \( V_0 \) are the surface area and the volume of the core respectively, \( F_1 \), \( F_2 \), \( F_3 \) are functions given in Kihara's paper and have recently been extended by Connolly and Kandelic. Considering only first order deviation we obtain for all shapes of cores

\[ B = \frac{2\pi}{3} \rho_0^3 \left[ P_3(z) + xP_2(z) \right] \]

with

\[ x = \frac{M_0}{2\pi \rho_0^2} \]

(10)

From equations (8) and (10) we obtain

\[ \frac{M_0}{2\pi \rho_0^2} = 7.0 \omega + 0.24 \]  

(11)

This result together with the fact that \( V_0 \) and \( S_0 \) are expressable in terms of \( M_0 \) for a particular shape of core enables us to write Eq.(9) depending parametrically on \( \omega \). By comparison between this function (9) and the experimental values of \( B = B(T) \) a new set of parameters for the Lennard-Jones type potential function can be obtained.

For each particular substance with fixed \( \omega \), equation (9) depends on \( U_0 / k \) and \( \rho_0 \) only. By plotting this theoretical expression for \( B(T) \) versus \( \log \frac{BT}{U_0} \) on transparent paper for different given values of \( \rho_0 \) a family of curves is obtained which can be superimposed over a graph of the experimental curve \( B(T) \) versus \( \log T \). This gives \( \rho_0 \) and \( U_0/k \).
This criterion was applied to the particular molecules using values of $\omega$ tabulated in paper II.

The various transformations which led up to equation (8) were carried out only through the first order in $\omega$. We tested the adequacy of equation (8) for large $\omega$ values by direct comparison of the calculated second virial coefficient curves for particular cores corresponding to large $x$ values with the curves from calculated equation (2) by use of the corresponding $\omega$. While this test was not extremely precise, it showed that the linear development was adequate in the range of $\omega$ values here considered and for the present accuracy of experimental data.

We consider first molecules with zero or negligible dipole or quadrupole electric moments.

1) Tetrahedral cores:

$\delta$: Length of one edge of the tetrahedron

$M_0 = 5.733 \delta$

$S_0 = 1.732 \delta^2$

$\beta = \frac{1}{2.737} \rho_0 x$

$x = 7.0 \omega + 0.24$

$V_0 = 0.1173 \delta^3$

$B = \rho_0 \frac{3\pi}{3} \frac{\pi}{3} F_3(Z) + \frac{2\pi}{3} \pi F_2(Z) + 0.5802 x^2 F_1(Z) + 0.3911 x^3$

The distance $d$ from center to vertex of the tetrahedron is given by

$$d = \frac{\delta}{2 \sin \left(\frac{\pi}{2}\right)}$$

$\alpha$ is $\text{H-C-H}$ bond angle in methane. Results of the calculations together with Kihara’s values are given in Table II. For comparison the C-H distance in methane is 1.09 Å and the C-F distance in $\text{CF}_4$ is 1.32 Å.
### TABLE II

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\rho_0 , \text{Å}$</th>
<th>a</th>
<th>Kihara</th>
<th>b</th>
<th>Present Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>378</td>
<td>1.92</td>
<td>3.15</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>226</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td>1.09</td>
<td>0.596</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>CF$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>372</td>
<td>2.48</td>
<td></td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>350</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.32</td>
<td>1.32</td>
<td></td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>

a - Reference (3)


Figure 1 shows the curves for methane corresponding to our parameters of Table II and to those of Kihara. Although both curves fit the data above 273°K, the curve based upon the acentric factor agrees much better with the recent experimental data of Thomales$^5$ at lower temperatures.
11) Hexagonal Cores

\[ a: \text{length of one side of the hexagon} \]

\[ u_0 = 3w^2 \]

\[ s_0 = 5.2 \, \text{e}^2 \]

\[ b = \frac{2}{\sqrt{3}} \, \text{x} \]

\[ B = \rho_0^3 \left[ \frac{2\pi}{3} F_3 (z) + \frac{2}{3} \pi x F_2 (z) + 0.6057 x^2 F_1 (z) + 0.0438 x^3 \right] \]

At the time Kihara's work was published (1953) there were not sufficient observed values of the second virial coefficient for benzene to determine both \( u_0 \) and \( \rho_0 \). His value of \( \rho_0 \) is taken from the lattice constant of graphite. Recently, however, Andon et al.\(^6\) reported measurements on the second virial coefficient for benzene between 67.1 and 164.6\(^\circ\)C. By use of their results together with the older values of Francis and McGlashan\(^7\) we have calculated both \( \rho_0 \) and \( u_0 \) from second virial coefficient data only.

Results are given in Table III. For comparison the C-C distance in benzene is 1.397\(\text{\AA} \).

---


TABLE III

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kihara</th>
<th>Present Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_0$</td>
<td>3.4 Å</td>
<td>3.0 Å</td>
</tr>
<tr>
<td>$\alpha_0/\kappa$</td>
<td>830 °K</td>
<td>990 °K</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1.93 Å</td>
<td>1.16 Å</td>
</tr>
</tbody>
</table>

(a) From the lattice constant of graphite

(b) From second virial coefficient data
iii) Spherical core

If we assign spherical core for $\text{CH}_4$, which is a permissible approximation considering its rapid and relatively free rotation, we obtain for the radius of the spherical core $a = 0.21 \, \text{ Å}$.

We also consider the globular-type molecule, neopentane, and assume a spherical core.

$$a: \text{radius of the sphere} \quad a = \frac{1}{6} \rho_0 x$$

$$B = \frac{2}{3} \pi \rho_0^3 \left[ F_3(Z) + xF_2(Z) + \frac{1}{3} \frac{2}{5} x^2 F_1(Z) + \frac{x^3}{27} \right]$$

There results:

$$\rho_0 = 3.96$$

$$\frac{u_0}{k} = 590 \, \text{Å}$$

$$a = 1.06 \, \text{Å}$$

C-C bond length = 1.536 Å

iv) Thin rod shaped cores

We consider in this case $\text{N}_2$ and $\text{CO}_2$.

$$M_0 = \pi l, \quad l = \frac{2}{3} \rho_0 \left( 7.0 \omega + 0.24 \right)$$

where $\ell$ is the length of the rod.

$$B = \frac{2\pi}{3} \rho_0^3 \left[ F_3(Z) + xF_2(Z) + \frac{1}{6} \frac{2}{5} x^2 F_1(Z) \right]$$

The results obtained are listed in Table IV. For comparison the N-N distance is 1.095 Å in $\text{N}_2$ and the O-O distance in $\text{CO}_2$ is 2.32 Å. The cores for $\text{N}_2$ and $\text{CO}_2$ seem peculiarly large, particularly so for $\text{CO}_2$.

The fact that equation (11) gives non-zero core constants for $\omega = 0$ indicates that there is some small core effect even in the simple fluids ($\text{Ar}$, $\text{Kr}$, etc.). It is then reasonable to consider cylindrical cores in $\text{N}_2$ and $\text{CO}_2$ with the radius of the cylinder $a$ obtained from the relationship between $a$ and $\rho_0$ for simple fluids.
From (10) and (11) for \( \omega = 0 \) one gets a spherical core radius \( a = 0.04 \rho_0 \).

This relationship for \( a \) enters the expressions for a cylindrical core which are

\[
M_0 = \pi (ma + \ell) = \frac{2\pi}{3} x_0^3, \quad S_0 = 2\pi a (a + \ell)
\]

\[
V_0 = \pi a^3, \quad \ell = \frac{2}{3} x_0^3 - ma
\]

One then obtains

\[
B = \frac{2\pi}{3} \rho_0^3 \left[ \frac{F_3(z) - 0.010 F_1(z) - 0.0003 + [F_2(z) + 0.080 F_1(z)]}{6} + \left( \frac{1}{6} F_1(z) + 0.0133 \right) x^2 \right]
\]

The results considering cylindrical core are also given in Table IV.
### TABLE IV

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kihara a</th>
<th>Kihara b</th>
<th>Present Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>3.47</td>
<td></td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td></td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td></td>
<td>1.19</td>
</tr>
<tr>
<td>a A</td>
<td>0.00</td>
<td></td>
<td>0.00</td>
</tr>
</tbody>
</table>

| CO₂      | 3.36     | 3.7      | 2.72         | 2.6          |
|          | 279      | 2.79     | 4.00         | 4.05         |
|          | 2.20     | 2.30     | 3.29         | 2.82         |
| a A      | 0.00     | 0.00     | 0.00         | 0.10         |

* a. Reference (3)

These two linear molecules have electric quadrupole moments. The order of magnitude of quadrupole-quadrupole interaction energy is by no means negligible compared to pure London dispersion energy. The contribution to the second virial coefficient coming from quadrupole-quadrupole interactions should also be considered.

An attempt was made to extend the core model for angular dependent potentials rigorously to include the quadrupole effect, but the mathematical complexity of the problem involving non-spherical cores makes an exact and rigorous treatment unduly complex.

An estimate of the electrostatic quadrupole-quadrupole effect was made for linear molecules in the following manner. The distance between quadrupoles, which are assumed to be at molecular centers, is $r$ and this distance must be related to $\rho$. Strictly, this relationship involves the orientation of each molecule, but for linear molecules one can show that the equation

$$r = \rho + \frac{a}{2} + a$$

should be a good approximation. This equation corresponds to the orientation yielding the most negative quadrupole-quadrupole energy and is also a reasonable average for all orientations. The effective spherically symmetrical potential function for quadrupole interaction obtained by a statistically weighed average over the angles with relationship (14) above was combined with the Lennard-Jones type Kihara potential to yield a function of $\rho$ that was integrated graphically to obtain $B$. The result of this integration was compared with the one obtained for the Kihara potential alone. The corresponding virial coefficients at 300°K for CO$_2$ differed by approximately 15%.

---

The numerical value of the quadrupole moment for CO\textsubscript{2} was taken from the measurement by Smith and Howard.\textsuperscript{9}

With this estimate of the quadrupole interaction contribution to the virial coefficient we then studied this effect in connection with the core size. The results obtained by Pople\textsuperscript{10} allow one to write the virial coefficient for molecules with permanent quadrupole moments as

\[
B(T) = \frac{2}{3} \mu^2 r_0^3 \left[ F(y) - \frac{7}{320} \left( \frac{\Theta^2}{U_0 - 0} \right)^2 H_{10}(y) \right]
\]

where \( r_0 \) is the intermolecular distance at which the non-angular part of the potential energy function vanishes. \( U_0 \) is the most negative value of the same part of the potential,

\[
y = 2 \left( \frac{U_0}{\mu^2} \right)^{\frac{3}{2}}
\]

\( \Theta \) is the quadrupole moment\textsuperscript{11} and \( H_{10}(y) \) is a function expressable as a series and known in tabular form.\textsuperscript{12}


\textsuperscript{10} Pople, J.A. Proc. Roy. Soc. A\textsuperscript{221}, 496(1954) and ibid. A\textsuperscript{221}, 508(1954).

\textsuperscript{11} The quadrupole moment definition used in this paper is

\[
\Theta = \Sigma_{i=1} Z_i^2 - x_i^2 \text{ where } Z_i \text{ is measured along the molecular axis}
\]

\textsuperscript{12} Tables for \( H_{10}(y) \) are given by A.D. Buckingham and J.A. Pople, Trans. Faraday Soc. \textbf{51}, 1173, (1955).
We fitted a third degree polynomial to the tabulated values of \( H_{10}(y) \) and by transformation to our set of variables obtained

\[
H(Z) = 0.07989 - 0.78915Z + 0.05201 Z^2 - 2.40473 Z^3
\] (15)

If we define the dimensionless parameter

\[
s = \left( \frac{\sigma^2}{u_0^2} \right)
\]

depending on the quadrupole moment, we can write for the second virial coefficient including first order core and quadrupole effects

\[
B = \frac{\pi}{3} \rho_0 \delta \left[ P_3(Z) + x P_2(Z) + s H(Z) \right]
\] (16a)

or in reduced form

\[
\frac{B}{V_B} = \left[ \frac{B}{V_B} \right]_0 + x \left[ \frac{\partial}{\partial x} \left( \frac{B}{V_B} \right) \right]_0 + s \left[ \frac{\partial}{\partial s} \left( \frac{B}{V_B} \right) \right]_0
\] (16b)

As we want to compare equation (16b) with the empirical equations (4) and (6), we reduced the function \( H(Z) \) to Boyle point basis using the definition of Boyle volume given by (3). The result is

\[
\left[ \frac{\partial}{\partial s} \left( \frac{B}{V_B} \right) \right]_0 = -0.1020 + 0.1105 \left( \frac{T_B}{T} \right) + 0.0842 \left( \frac{T_B}{T} \right)^2 - 0.0932 \left( \frac{T_B}{T} \right)^3
\] (17)

Comparing equation (17) with the corresponding equation for \( x \), equation 15b in paper I, one finds that in the low temperature range, where the quadrupole effect is most marked the relationship

\[
\left[ \frac{\partial}{\partial s} \left( \frac{B}{V_B} \right) \right] / \left[ \frac{\partial}{\partial x} \left( \frac{B}{V_B} \right) \right] = 3.2
\] (18)

is a fair approximation.

Substitution of equation (18) in (16b) and use of equation (11) yields

\[
x + 3.2s = 7.00 + 0.24
\] (19)
This relationship between core size, quadrupole moment and acenric factor enables us to write equation (16a) in terms of \( \omega \). As the parameter \( \beta \) depends on \( \alpha_0 \) and \( \Upsilon_0 \) by definition, a successive approximation method is necessary for the evaluation of \( \alpha_0 \) and \( \Upsilon_0 \). The results obtained for \( \text{CO}_2 \) and \( \text{N}_2 \) are listed in Table V. These results show that when the quadrupole effect is considered the sizes of the cores are again smaller than the ones assumed by Kihara from molecular structure information. A few years after Kihara's work was published a measurement of the second virial coefficient for \( \text{CO}_2 \) at low temperatures was reported. \(^{14}\) These values, together with the older results reported by Schäfer and MacCormack and Scheneider \(^{15}\) are shown in Figure 2. A distinctly better fit to this experimental data is obtained from the parameters of Table V of this paper than from the expression given by Kihara.


<table>
<thead>
<tr>
<th></th>
<th>e.e.e.u.</th>
<th>S</th>
<th>$p_0$ Å</th>
<th>$u_0 /K$</th>
<th>0K Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>$1.488 \times 10^{-26}$</td>
<td>0.05</td>
<td>3.60</td>
<td>115</td>
<td>0.86</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>$3.12 \times 10^{-26}$</td>
<td>0.33</td>
<td>3.42</td>
<td>270</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Exp. Dist. $H-H = 1.095$ Å, $O-O = 2.32$ Å
Discussion

In paper I the intermolecular potential to be expected for a globular molecule was considered and it was concluded that the Kihara model core should be considerably smaller than the polarizable electron cloud of the molecule. Indeed the radius of a Kihara model core was found to be only one half of the radius of an equivalent sphere of uniformly polarizable electron cloud. In view of these results the cores found above seem quite reasonable. Thus in \( \text{CF}_4 \) and \( \text{C}(\text{CH}_3)_4 \) the cores extend about \( 2/3 \) of the way to the \( F \) or \( C \) (methyl) nuclei, respectively. Methane has a very small core since all of the polarizable electrons are partially centered on the single carbon atom. The hexagonal core for benzene extends almost to the ring carbon atoms. The cores chosen by Kihara in 1953 seem to have been selected rather arbitrarily; for example his core for methane extended to the hydrogen nuclei whereas in benzene the core extended only to the mid-points of the \( C-H \) bonds. Consequently it is not surprising that our results differ rather substantially. In the case of methane the results in Figure 1 show clearly that the core selected from the acentric factor is the correct one to fit the wide range of data now available.

The tetrahedral molecules have zero electric quadrupole moment by symmetry but the linear molecules \( \text{H}_2 \) and \( \text{CO}_2 \) have significant moments. While our treatment including the quadrupole effect is only an approximate one for the model, it does show that the linear cores are thereby reduced to reasonable sizes.

With these results as a guide one should be able to estimate reasonable core sizes for other molecules if the acentric factor or equivalent data
are unavailable. Conversely, the acentric factor and other data may be used, as has been illustrated in this paper, to derive an intermolecular potential for use in other calculations.

This work has been performed under the auspices of U.S. Atomic Energy Commission. The aid of a Fulbright Travel Grant to one of us (F.D.) is gratefully acknowledged.
Figure Legends

Fig. 1. The second virial coefficient ($\hat{A}^3$/molecule) for methane. The curves are theoretical; the points experimental. Solid circles show the experimental values (Michels and Nederbragt$^a$) available to Kihara. Recent measurements of Thomales$^b$ are shown as open circles.

$^a$A. Michels and G. W. Nederbragt, Physics 3, 569 (1936).

Fig. 2. The second virial coefficient ($\hat{A}^3$/molecule) for CO$_2$. The curve is calculated using the results of this paper. Solid circles corresponds to MacCormack and Scheneider measurements$^{14}$ triangles to Cook$^{12}$ and squares to Schafer$^{13}$.