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

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

by

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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 CH_4, CF_4, $C(CH_3)_4$, C_6H_6 and N_2 are reasonable in view of semi-quantitative theoretical expectations, but the core for CO_2 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 CO_2 on this model including the quadrupole moment is of a reasonable size.

A series of recent papers[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.[2]

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1 Papers in the series will be cited by the roman numerals as follows: I K.S. Pitzer, J. Am. Chem. Soc 77 3427(1955); II K.S. Pitzer, D.Z. Lippmann, R.F. Curl, Jr., C.M. Huggins and D.E. Petersen, ibid 77 3433 (1955); III K.S. Pitzer and R.F. Curl Jr. ibid 79 2369(1957); IV R.F. Curl Jr., and K.S. Pitzer, Ind. Eng. Chem. 50 265(1958); V K.S. Pitzer and G.O. Hultgren, J. Am. Chem. Soc. 80 4793(1958).

2 J.O. Hirschfelder, F.T. McClure and I.F. Weeks, J. Chem. Phys. 10 201 (1942); J.S. Rowlinson, Trans. Faraday So. 45 974 (1949).

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[3] 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

$$U = U_0 \left[\left(\frac{\rho_0}{\rho} \right)^{12} - 2 \left(\frac{\rho_0}{\rho} \right)^{6} \right] \tag{1}$$

where ρ is the shortest distance between cores and ρ_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[4] and methane[5] as well as the general considerations of the intermolecular potential in paper I.

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

[4] J.F. Connolly, G.A. Kandalic, Phys. of Fluids 3 463(1960).

[5] G. Thomales, Nature, 187 229 (1960)

The equation for the second virial coefficients given in III in dimensionless form is

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega \frac{B^{(1)}P_c}{RT_c} \tag{2}$$

where

$$\frac{B^{(0)}P_c}{RT_c} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \tag{2a}$$

$$\frac{B^{(1)}P_c}{RT_c} = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} \tag{2b}$$

and

$$\omega = -\log P_r - 1.000 \tag{2c}$$

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

$$V_B = \left[T \frac{dB}{dT} \right]_{T = T_B} \tag{3}$$

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

$$\frac{B^{(0)}}{V_B} = 0.8736 - 0.7512\left(\frac{T_B}{T}\right) - 0.1185\left(\frac{T_B}{T}\right)^2 - 0.0039\left(\frac{T_B}{T}\right)^3 \tag{4}$$

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 ω as well as the critical constants. Hence the criterion for the Boyle point must be reapplied to the

general equation (2) and yields

$$T_B = \frac{2.656\ T_c}{(1+1.028\omega)} \qquad \text{and} \quad V_B = \left(\frac{RT_c}{P_c}\right)(0.1651 + 0.1981\omega)$$

Now the second virial coefficient is

$$B = B^{(0)} + \omega B^{(1)} + \text{----} \tag{5}$$

$$\text{with } \frac{B^{(1)}}{V_B} = -0.6087 + 1.11760\left(\frac{T_B}{T}\right) - 0.5299\left(\frac{T_B}{T}\right)^2 - 0.0386\left(\frac{T_B}{T}\right)^3 - 1.79 \times 10^{-5}\left(\frac{T_B}{T}\right)^8 \tag{6}$$

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

$$\frac{B}{V_B} = \left[\frac{B}{V_B}\right]_0 + x\left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right)\right]_{x=0} \tag{7}$$

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 (T_B / T). 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 Ar, Kr, 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 $x = 7.0\omega$ and shows good agreement over the range of interest.

TABLE I

T_B/T	$-\frac{B^{(1)}}{V_B}$	$-7.0\left[\frac{\partial}{\kappa}\left(\frac{B}{V_B}\right)\right]_{\kappa=0}$
0.8	0.027	0.026
1.0	0.001	0.002
1.5	0.168	0.166
2.0	0.690	0.690
2.5	1.611	1.625
3.0	3.010	3.020

This comparison of equations (5) and (7) has resulted in agreement provided

$$x = 7.0\,\omega + 0.24 \tag{8}$$

Kihara's general expression for the second virial coefficient is

$$B = \frac{2\pi}{3}\rho_0^3 F_3(Z) + M_0\rho_0^2 F_2(Z) + \left(S_0 + \frac{M_0^2}{4\pi}\right)\rho_0 F_1(Z) + \left(V_0 + \frac{M_0 S_0}{4\pi}\right) \tag{9}$$

where $Z = \frac{U_0}{kT}$, 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[3] and have recently been extended by Connolly and Kandalic.[4] Considering only first order deviation we obtain for all shapes of cores

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

with

$$x = \frac{3M_0}{2\pi\rho_0} \tag{10}$$

From equations (8) and (10) we obtain

$$\frac{3M_0}{2\pi\rho_0} = 7.0\,\omega + 0.24 \tag{11}$$

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 ω. 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 ω, equation (9) depends on U_0 / k and ρ_0 only. By plotting this theoretical expression for $B(T)$ versus $\log \frac{kT}{U_0}$ on transparent paper for different given values of ρ_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 ρ_0 and U_0/k.

This criterion was applied to the particular molecules using values of ω tabulated in paper II.

The various transformations which led up to equation (8) were carried out only through the first order in ω. We tested the adequacy of equation (8) for large ω 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 ω. While this test was not extremely precise, it showed that the linear development was adequate in the range of ω 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:

ℓ: Length of one edge of the tetrahedron

$$M_0 = 5.733\,\ell$$

$$S_0 = 1.732\,\ell^2 \qquad \ell = \frac{1}{2.737}\,\rho_0 x \qquad x = 7.0\,\omega + 0.24$$

$$V_0 = 0.1178\,\ell^3$$

$$B = \rho_0^3\left[\frac{2\pi}{3}F_3(Z) + \frac{2\pi}{3}xF_2(Z) + 0.5802\,x^2F_1(Z) + 0.3911x^3\right]$$

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

$d = \dfrac{\ell}{2\sin\left(\frac{\alpha}{2}\right)}$ α is 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 CF_4 is 1.32 Å.

TABLE II

Molecule		Kihara a	Kihara b	Present Work
CH_4	ρ_0 Å	1.92	3.15	3.75
	$\frac{U_0}{k}$ °K	378	226	175
	d Å	1.09	0.596	0.28
CF_4	ρ_0 Å	2.48		3.08
	$\frac{U_0}{k}$ °K	372		350
	d Å	1.32		1.01

a - Reference (3)

b - T. Kihara and S. Koba, J. Phys. Soc. Japan 14 247, (1959)

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.

ii) Hexagonal Cores

ℓ: length of one side of the hexagon

$$M_0 = 3\pi\ell$$

$$S_0 = 5.2\,\ell^2$$

$$\ell = \frac{2}{9}x$$

$$B = \rho_0^3\left[\frac{2\pi}{3}F_3(Z) + \frac{2}{3}\pi x F_2(Z) + 0.6057\,x^2F_1(Z) + 0.0428x^3\right]$$

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 ρ_0. His value of ρ_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°C. By use of their results together with the older values of Francis and McGlashan[7] we have calculated both ρ_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 1.397Å.

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6 R.J.L. Andon, J.D. Cox, E.F. Herington and J.F. Martin, Trans-Faraday Soc. 53, 1074(1957); J.D. Cox and R.L. Andon, ibid. 54,1622(1958).

7 P.G. Francis, M.L. McGlashan, S.D. Hamann and W.J. McNamamey, J. Chem. Phys. 20,1341(1952).

TABLE III

Molecule		Kihara	Present Work
C_6H_6	ϕ_0	3.4 Å (a)	3.0 Å (b)
	U_0/k	830 °K	990 °K
	ℓ	1.93 Å	1.16 Å

(a) From the lattice constant of graphite

(b) From second virial coefficient data

iii) Spherical core

If we assign spherical core for CH_4, which is a permissible approximation considering its rapid and relatively free rotation, we obtain for the radius of the spherical core $a = 0.21$ Å.

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

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

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

There results:

$\rho_0 = 3.96$

$\frac{U_0}{k} = 590\ ^\circ K$

$a = 1.06$ Å $\qquad$ C-C bond length = 1.536 Å

iv) Thin rod shaped cores

We consider in this case N_2 and CO_2.

$M_0 = \pi\ell$, $\ell = \frac{2}{3}\rho_0(7.0\,\omega + 0.24)$ where ℓ is the length of the rod.

$$B = \frac{2\pi}{3}\rho_0^3\left[F_3(Z) + xF_2(Z) + \frac{1}{6}x^2F_1(Z)\right] \tag{12}$$

The results obtained are listed in Table IV. For comparison the N-N distance is 1.095 Å in N_2 and the O-O distance in CO_2 is 2.32 Å. The cores for N_2 and CO_2 seem peculiarly large, particularly so for 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 (Ar, Xe, etc.). It is then reasonable to consider cylindrical cores in N_2 and CO_2 with the radius of the cylinder a obtained from the relationship between a and ρ_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

$$M_0 = \pi\,(\pi a + \ell) = \frac{2\pi}{3}\,x\rho_0,\quad S_0 = 2\pi\,a(a + \ell)$$

$$V_0 = \pi a^2 \ell,\quad \ell = \frac{2}{3}\,x\rho_0 - \pi a$$

One then obtains

$$B = \frac{2\pi}{3}\,\rho_0^3 \Big[\, F_3(Z) - 0.010F_1(Z) - 0.0003 + [F_2(Z) + 0.080\,F_1(Z)]x + [\,\tfrac{1}{6}\,F_1(Z) + 0.0133\,]\,x^2 \Big]$$

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

TABLE IV

Molecule		Kihara [a]	Kihara [b]	Present Work: Thin rod core	Present Work: Cylindrical core
N_2	ρ_0 Å	3.47		3.40	3.30
	U_0/K °K	124		132	125
	ℓ Å	1.09		1.19	0.73
	a Å	0.00		0.00	0.13
CO_2	ρ_0 Å	3.36	3.7	2.72	2.6
	U_0/K °K	279	2.79	400	405
	ℓ Å	2.20	2.30	3.29	2.82
	a Å	0.00	0.00	0.00	0.10

a. Reference (3)

b. Kihara, T. J. Phys. Soc. Japan 6 289 (1951).

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 ρ. Strictly, this relationship involves the orientation of each molecule, but for linear molecules one can show that the equation

$$r = \rho + \ell/2 + a \tag{14}$$

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[8] with relationship (14) above was combined with the Lennard-Jones type Kihara potential to yield a function of ρ 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%.

[8] For details of the averaging process see: J.O. Hirschfelder, C.F. Curtiss and R.B. Bird "Molecular Theory of Gases and Liquids" John Wiley and Sons. New York 1954 p. 27.

The numerical value of the quadrupole moment for CO_2 was taken from the measurement by Smith and Howard.[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[10] allow one to write the virial coefficient for molecules with permanent quadrupole moments as

$$B(T) = \frac{2}{3}\pi N r_0^3\left[F(y) - \frac{7}{320}\left(\frac{\Theta^2}{U_0 r_0^5}\right)^2 H_{10}(y)\right]$$

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,

$$y = 2\left(\frac{U_0}{kT}\right)^{\frac{1}{2}}$$

Θ is the quadrupole moment[11] and $H_{10}(y)$ is a function expressable as a series and known in tabular form.[12]

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[9] Smith, W.V. and Howard R. Phys. Rev. 79 132(1950).

[10] Pople, J.A. Proc. Roy. Soc. A221 498(1954) and ibid. A221 508(1954).

[11] The quadrupole moment definition used in this paper is

$\Theta = \Sigma_i e_i(Z_i^2 - x_i^2)$ where Z_i is measured along the molecular axis

[12] Tables for $H_{10}(y)$ are given by A.D. Buckingham and J.A. Pople, Trans. Faraday Soc. 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

$$H(Z) = 0.07089 - 0.78915Z = 0.05201\ Z^2 - 2.40478\ Z^3 \tag{15}$$

If we define the dimensionless parameter

$$s = \left(\frac{\sigma^2}{U_0 \rho_0^5}\right)$$

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

$$B = \frac{2\pi}{3}\rho_0^3\left[\ F_3(Z) + xF_2(Z) + sH(Z)\ \right] \tag{16a}$$

or in reduced form

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

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

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

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

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

is a fair approximation.

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

$$x + 3.2s = 7.0\omega + 0.24 \tag{19}$$

This relationship between core size, quadrupole moment and acentric factor enables us to write equation (16a) in terms of ω. As the parameter s depends on ρ_0 and U_0 by definition, a successive approximation method is necessary for the evaluation of ρ_0 and U_0. The results obtained for CO_2 and N_2 [13] 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 CO_2 at low temperatures was reported.[14] These values, together with the older results reported by Schäfer and MacCormack and Scheneider[16] 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.

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[13] Numerical value for the quadrupole moment of N_2 is taken from W. Gordy, W.V. Smith and R. Trambarulo "Microwave Spectroscopy", John Wiley and Sons, Inc., New York 1953 p.345.

[14] D. Cook, Can. Jour. of Chem. 35 369 (1957).

[15] K. Schäfer, Z. Phys. Chem. B36 85 (1937).

[16] K.E. MacCormack and W.G. Scheneider, J. Chem. Phys. 18 1269 (1950)

TABLE V

	Θ e.s.u.	S	ρ_0 Å	U_0/K °K	ΔÅ
N_2	$1.488.10^{-26}$	0.05	3.60	115	0.86
CO_2	$3.12.10^{-26}$	0.33	3.42	270	1.73

Exp. Dist. N-N = 1.095 Å, O-C-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 CF_4 and $C(CH_3)_4$ 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 N_2 and 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 ($Å^3$/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.

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[a] A. Michels and G. W. Nederbragt, Physics 3, 569 (1936).
[b] G. Thomales, Nature 187, 229 (1960).

Fig. 2. The second virial coefficient ($Å^3$/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)]

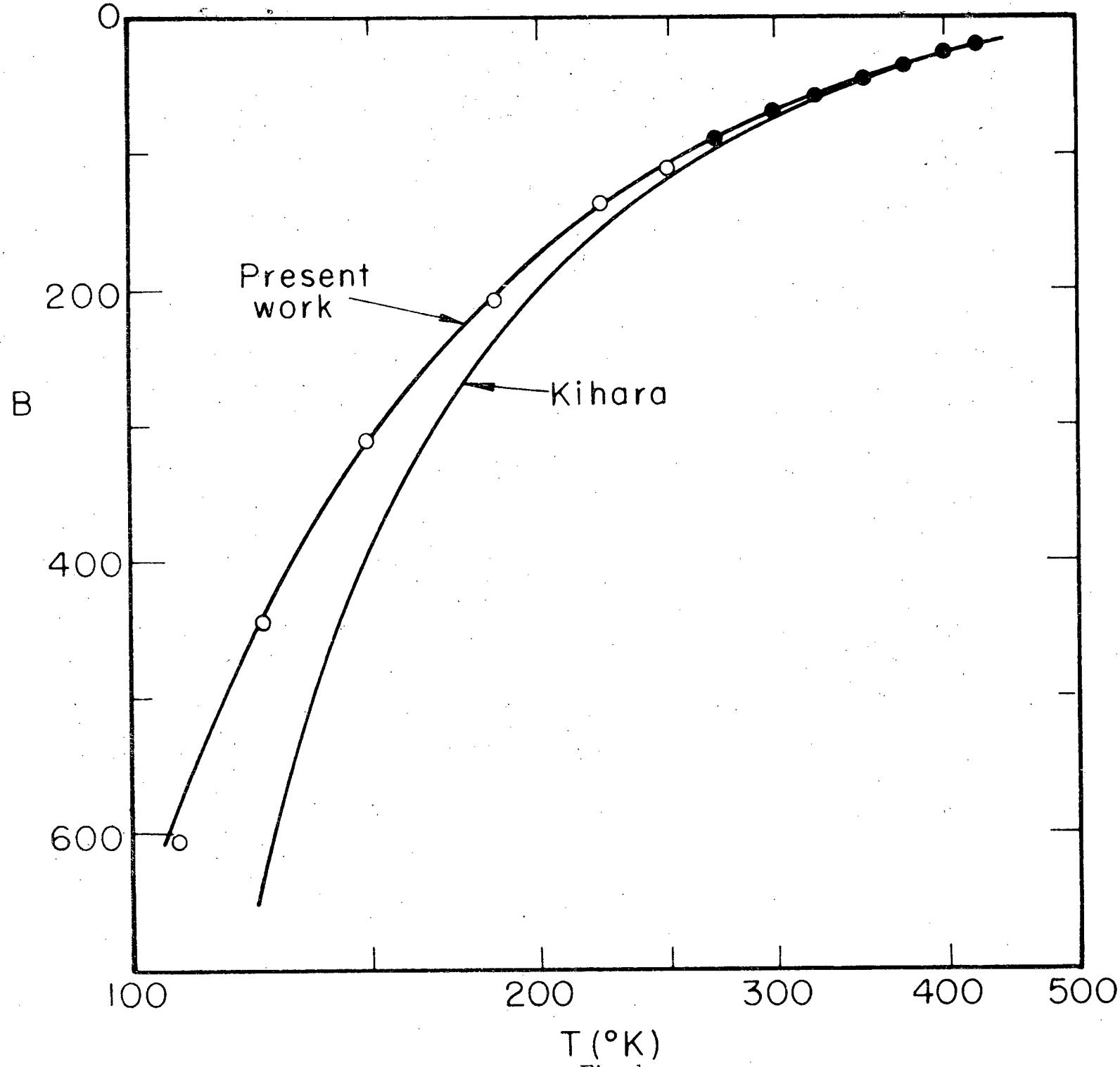

Fig. 1.

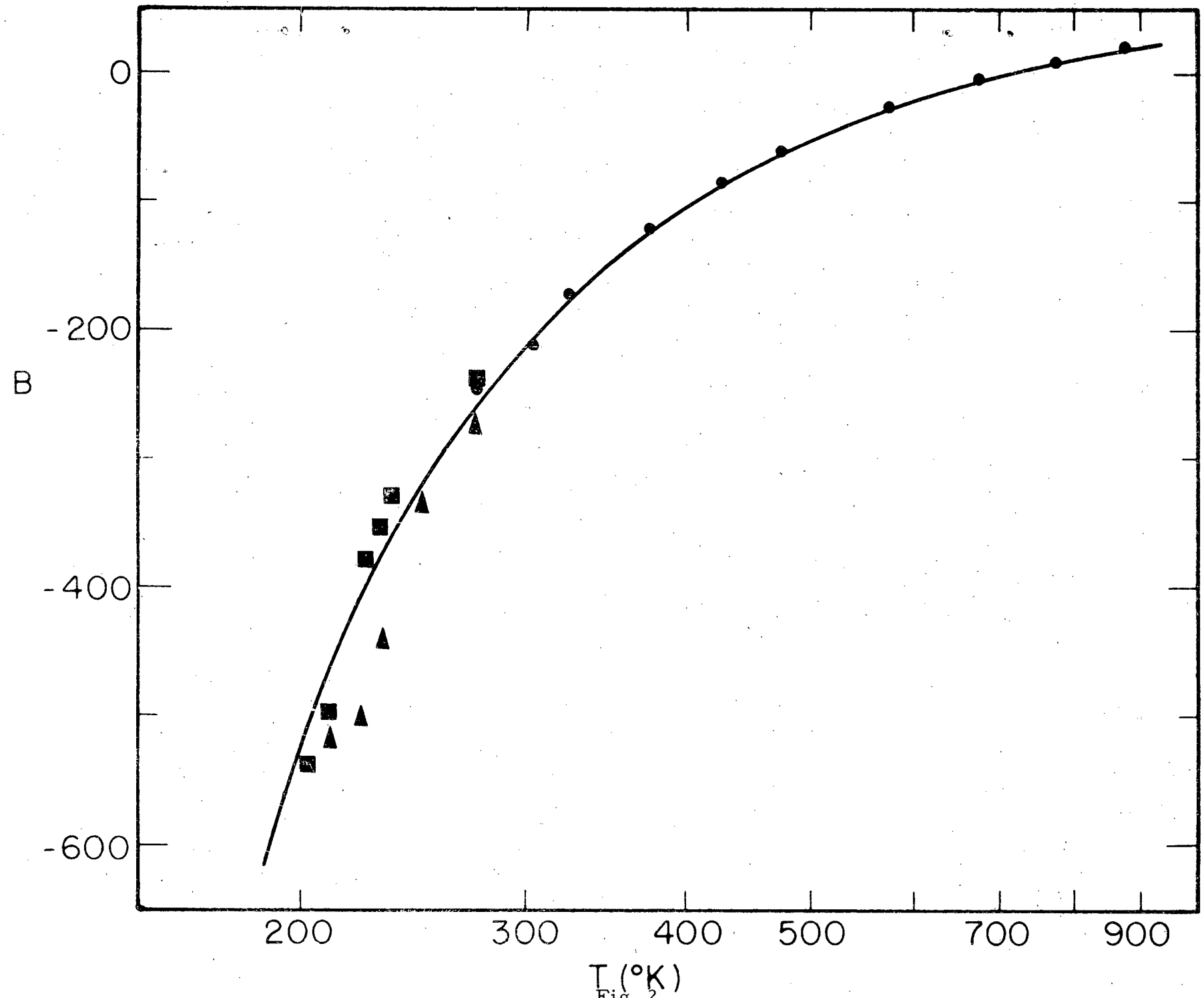

Fig. 2.