Kihara Parameters and Second Virial Coefficients For Cryogenic Fluids and Their Mixtures

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The volumetric properties of sixteen fluids of interest in cryogenic engineering have been used to calculate second virial coefficients over as large a temperature range as possible. These coefficients were then fitted to theoretical expressions based on the Kihara potential function. For helium, hydrogen, and neon quantum corrections were applied. For nitrogen, carbon dioxide, and acetylene corrections for quadrupole interactions were made. It was found that the theoretical expressions give an extremely good fit of all reliable experimental data. The theoretical expressions may therefore be used with confidence to predict volumetric behavior at very low temperatures where data are frequently unavailable.

With the aid of semiempirical mixing rules the theoretical expressions may be used to predict second virial coefficients for mixtures. Agreement with the very limited amount of experimental mixture data is satisfactory. Finally it is shown that calculations based on the Kihara potential may be employed to make useful predictions of phase equilibria such as the solubility of a solid in a compressed gas.

Recently there has been increasing interest in cryogenic processes, and present indications suggest that this interest will increase markedly in the near future. Accurate design of cryogenic equipment requires information on the thermodynamic properties of cryogenic fluids; this paper considers the volumetric properties of such fluids and their mixtures.

At moderate densities the volumetric properties of all fluids can be described by the virial equation of state truncated after the second virial coefficient:

$$\frac{Pv}{RT} = 1 + \frac{B(T)}{v} \qquad (1)$$

The main advantage of Equation (1) is that a precise physical significance can be given to B; it can be calculated exactly from statistical mechanics with an appropriate potential energy function. Furthermore it may be shown that Equation (1) is valid for mixtures and that the composition dependence of B is given by a quadratic function of the mole fractions. The applicability of the virial equation to mixtures makes it especially useful in certain types of phase equilibrium problems; an example of such an application is shown towards the end of the paper.

The potential function relates the potential energy of two molecules to the distance between them and, where necessary, to their relative orientation. Such a function contains several parameters, and since these parameters cannot be computed from first principles, they are customarily obtained from some macroscopic property. Of these the second virial coefficient itself is the most convenient; consequently some experimental information on the second virial coefficient is required to evaluate the potential function parameters. Now if experimental data are already available, why would one bother to evaluate the parameters? There are two important reasons for doing so. First the experimental data almost always apply to a limited temperature range, and thus it is desirable to compute the potential parameters (which are independent of temperature) in order to predict with confidence the second virial coefficient at some new temperature for which no measurements have been made. This is especially useful for cryogenic applications, since data at normal temperatures (which are relatively common) may then be used to predict the volumetric properties at very low temperatures where measurements are scarce. Secondly experimental data for mixtures are not plentiful. However if the potential parameters for the pure components in a mixture are known, it is possible to make good estimates of the potential parameters required for the mixture; thus it is a rather simple matter to use information on the pure compounds for predicting the properties of mixtures. This extension to mixtures is not limited to binaries but may be applied to mixtures of any number of components.

THE KIHARA POTENTIAL

Numerous potential functions have been proposed. The best known is that of Lennard-Jones which assumes that molecules are point centers whose force fields are spherically symmetric. As a result of these simplifying assumptions the Lennard-Jones potential gives a good representation of the second virial coefficient for only very simple molecules, and even for these the representation is accurate only for a restricted temperature range. Recently it was shown (*34*) that even for argon it is not possible to reproduce the highly accurate data of Michels (*22, 31*) with a unique set of Lennard-Jones parameters over the temperature range 133° to 423°K.

A considerable improvement over the Lennard-Jones potential has been suggested by Kihara (*15*) who replaces the point center model for a molecule by an impenetrable core whose dimensions are suggested by the geometry and internuclear distances of the molecule. Kihara retains the mathematical form of the Lennard-Jones potential, but the potential energy is now written not as a function of the distance between molecular centers but rather as a function of the minimum distance between molecular cores:

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

Using Equation (2) and the methods of statistical mechanics Kihara derives the second virial coefficient:

$$\frac{B}{N} = \frac{2\pi}{3}\rho_0^3F_3 + M_0\rho_0^2F_2 + \left(S_0 + \frac{M_0^2}{4\pi}\right)\rho_0F_1 + \left(V_0 + \frac{M_0S_0}{4\pi}\right) \quad (3)$$

The parameters M_0, S_0, and V_0 may be calculated directly from the size and shape of the core. The core may be a one, two, or three dimensional body, but it must be convex. An extensive tabulation of the functions F_1, F_2, and F_3 is given by Connolly (*5*); these functions have the argument z. The function F_3 corresponds to the Lennard-Jones potential; in the limiting case of a vanishing core M_0, S_0, and V_0 are all zero, and Kihara's result as given in Equation (3) reduces to that previously given by Lennard-Jones (*12*).

EXPERIMENTAL DATA

The data sources for the experimental second virial coefficients of pure substances are given in Table 1. The most extensive source of such data is that of Michels and co-workers at the Van der Waals laboratory in Amsterdam. For propane and acetylene no good experimental data were available, and the Pitzer-Curl empirical equation (*39*) was substituted for these substances. The results of Schäfer (*43*) for acetylene scatter badly and were considered unreliable. The Pitzer-Curl empirical equation gives excellent agreement with the available experimental results, especially for temperatures greater than about 0.6 of the critical temperature. For example in the case of nitrogen the maximum deviation between the second virial coefficients given by the Pitzer-Curl equation and the second virial coefficients observed by the investigators listed in Table 1 is 5 cc./mole.

The experimental data of Michels and co-workers (Amsterdam), when available, were favored over those of most of the other work on second virial coefficients. The scatter of the Amsterdam data was of the order of 0.1 cc./mole, whereas the scatter of most of the other work was of the order of 1 to 5 cc./mole. This is not to say that the Amsterdam data are the best, but since they seldom deviate more than a few cubic centimeters from the other experimental data, the fitted theoretical curve not only agrees within about 0.2 cc./mole with the Amsterdam data but is a good average for all other available experimental data as well.

FITTING OF KIHARA POTENTIAL TO EXPERIMENTAL DATA

Kihara parameters were determined for sixteen fluids of common interest in cryogenic engineering. The sixteen fluids were divided into three groups: fluids possessing negligible permanent electric moments and requiring negligible quantum corrections; fluids exhibiting significant quantum effects, hydrogen, helium, and neon; fluids possessing a significant quadrupole moment, nitrogen, carbon dioxide, and acetylene.

Determination of Cores

The cores for all three classes of fluids were obtained by forming a reasonable convex core, the size of the core being determined from known internuclear separations of the constituent atoms of the molecule (*3*).

For the inert gases the only reasonable shape of the core is that of a sphere. Extensive and very accurate volumetric data are available for neon, argon, krypton, and xenon; therefore for these substances the radius of the spherical core was left as a third parameter (in addition to ρ_0 and U_0) to be determined by the best fit of the experimental data. The radii were found to be 0.15, 0.175, 0.21, and 0.25 Å. respectively for neon, argon, krypton, and xenon. For helium it was found that the extensive data are fit best when no core at all is used.

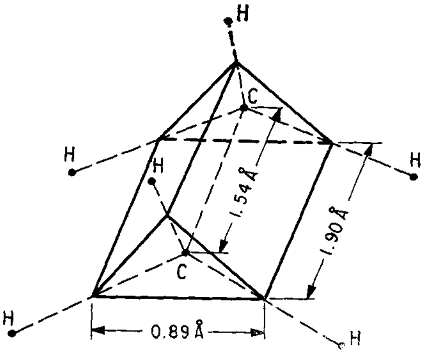

Fig. 1. Triangular prism core for ethane, six vertices formed by points midway between C-H nuclei.

For the hydrocarbons the optimum size of the core needed to fit the experimental data was somewhat smaller than the actual size of the molecule. This result is in agreement with similar conclusions reached by Danon and Pitzer (*10*). For example the core needed to fit the experimental data for methane was smaller than the tetrahedron formed by placing its four vertices at the four hydrogen atoms. The core actually used for methane was a tetrahedron one-third of the size of the above-described tetrahedron, with the length of one edge equal to 0.594 Å. For ethylene the core used was a rectangle of size 1.87 by 0.93 Å., where the four corners of the rectangle were placed midway between the C-H bonds. These cores then are somewhat smaller than those proposed previously by Kihara (*15*), Connolly and Kandalic (*5*), and Prausnitz and Keeler (*41*). These smaller cores give better agreement with experimental data, especially with some recent data at lower temperatures (*45*) where the second virial coefficient is most sensitive to core dimensions. It appears then that the impenetrable core of a molecule is not exactly given by the size of the molecule but by something somewhat smaller; in other words the molecules do not act as hard spheres nor as soft point centers but as something in between these two extremes. Illustrations of several cores are given in Figures 1, 2, and 3.

As molecules become larger and more complicated, it becomes more difficult to find an appropriate core, especially when rotation of bonds is possible. For example the pentagon core for propane is a rough attempt to describe the shape of the propane molecule. In fact the propane molecule is not flat and a more realistic core might have a concave surface, but for such a core the Kihara potential does not apply.

For propylene a pentagon core of the same shape as the propane core was used, but a size parameter was left to be determined by the best fit of the experimental data. The result was a core with the same shape as that for propane (Figure 2) but with all dimensions reduced by a factor of 0.824. Such a core does not take account of the asymmetry between the single and double bond of propylene, but any further refinement was considered unnecessary because the propylene molecule is not actually planar anyway.

A spherocylinder core was used for the diatomic molecules nitrogen, oxy-

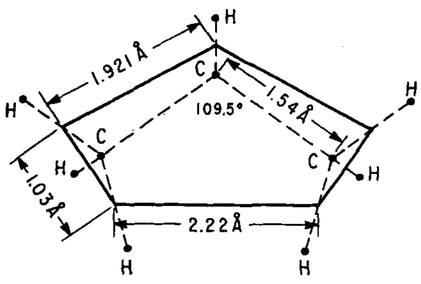

Fig. 2. Pentagon core for propane.

gen, and carbon monoxide. The spherocylinder is a cylinder capped with a hemisphere at each end, the radius of the cylinder being equal to the radius of each hemisphere. The length of the cylinder was set equal to the internuclear separation of the atoms, and its radius was determined by the best fit of the experimental data. The radii used were 0.10, 0.05, and 0.10 Å. for nitrogen, oxygen, and carbon monoxide.

A rod core was used for hydrogen, with length of 0.7416 Å., the same as the H—H separation. Since hydrogen atoms are very small, it is reasonable that for this molecule the core is a spherocylinder of zero radius.

For the linear molecule carbon dioxide a spherocylinder core was also used; the length of the cylinder was the O—O separation, 2.32 Å., and the radius was 0.15 Å. The same core was used for acetylene, the length of the cylinder being equal to the C—C separation, 1.204 Å., and radius equal to 0.532 Å.

Determination of ρ_o and U_o

The graphical procedure described by Prausnitz and Keeler *(41)* was used to evaluate the parameters ρ_o and U_o from the experimental data. When the size of the core was a third unknown parameter, the method was repeated for a number of core sizes until the optimum agreement was achieved.

When very precise experimental data, such as those of Michels, were available, a more accurate graphical procedure was used. For each experimental point, and with a certain core size, a plot of U_o vs. ρ_o was prepared; such a curve represents all possible combinations of U_o and ρ_o which satisfy the single experimental point. Then if the core size is adequate, all of these curves must intersect at a single point; this point is the optimum value of U_o and ρ_o. If the intersection of the curves is poor, additional core sizes must be tried until the intersection is satisfactory.

Parameters for the first class of fluids are given in Table 2. These parameters when used with Equation (3) give excellent agreement with experimentally measured second virial coefficients. For the older data the average deviation is about 2.0 cc./g.-mole, and the maximum deviation is less than 15 cc./g.-mole. However when comparison is made with Michels' data the average and maximum deviation are 0.2 and 0.8 cc./g.-mole respectively. A comparison of calculated and experimental second virial coefficients for methane is given in Figure 4.

Table 1. Data Sources

Substance	Temperature range, °K.	Reference
Argon	133-423	*22, 31, 37*
Krypton	273-573	*2*
Xenon	273-873	*1, 28, 48*
Oxygen	100-3,000	*13, 26, 35*
Carbon monoxide	200-3,000	*23*
Methane	108-423	*25, 45*
Ethylene	273-423	*21*
Ethane	273-423	*27*
Propylene	323-523	*30*
Propane	220-850	*39*
Helium	21-423	*32, 49*
Hydrogen	98-423	*20, 36*
Neon	65-673	*9, 13, 29*
Nitrogen	80-473	*13, 14, 33, 38, 46*
Carbon dioxide	204-573	*6, 18, 24, 43*
Acetylene	185-680	*39*

Fluids with Significant Quantum Effects

For fluids where the difference between classical and quantum mechanics is not negligible the second virial coefficient is written as

$$B = B_{\mathrm{Kihara}} + B_{\mathrm{quantum}} \qquad (4)$$

When quantum deviations are not too large, it is possible *(11)* to express them in terms of a power series in Λ^*:

$$B_{\mathrm{quantum}} = \frac{2}{3}\pi N \sigma^3 \left[\Lambda^{*2} B_I^* \left(\frac{1}{z}\right) + \Lambda^{*4} B^*_{II} \left(\frac{1}{z}\right) + \ldots - \Lambda^{*3} B_o^* \left(\frac{1}{z}\right) \right] \qquad (5)$$

where

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\,U_o}} \qquad (6)$$

The coefficients B_I^*, B_{II}^* . . ., and B_o^* are all functions of $(1/z)$, and these have been tabulated in reference *12.*

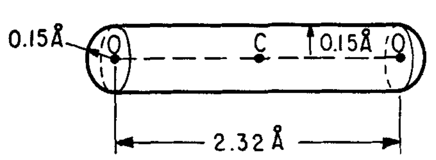

Fig. 3. Spherocylinder core for carbon dioxide.

Equation (5) applies only as a quantum correction for the Lennard-Jones potential which is the same as the Kihara potential in the special case of a vanishing core. As an approximation it is assumed that Equation (5) also applies as the quantum correction to the Kihara potential. Since σ is the separation of molecular centers when the potential energy is zero, it is related to the Kihara parameters by

$$\sigma = 2^{-1/6}\rho_o + \frac{M_o}{2\pi} \qquad (7)$$

Equation (7) is exact for a spherical core and an approximation for other cores.

The second virial coefficients for the so-called *quantum gases* are computed by Equations (3), (4), (5), (6), and (7). The quantum correction depends on the parameters U_o, ρ_o, M_o, and the mass of the molecule or atom. Since no additional unknown parameters are involved, the fitting of Equation (4) to the experimental data is carried out in the same way as described above.

For hydrogen there are also quantum corrections due to rotation. These corrections are in general considerably smaller than those due to translation *(12)*, and therefore, in view of the approximations already made in Equations (4) and (5), they were not considered here.

The required parameters for the quantum gases are given in Table 3. Figure 5 shows a comparison of experimental and computed results for hydrogen, and it is evident that the quantum corrections are considerable in this case. The data for hydrogen could of course have been fitted without any quantum corrections. However

Table 2. Kihara Parameters for Fluids Possessing Negligible Permanent Electric Moments and Requiring Negligible Quantum Corrections

Substance	Core	M_o, Å.	S_o, Å.^{2}	V_o, Å.^{3}	ρ_o, Å.	U_o/k, °K.
A	sphere	2.199	0.3848	0.02245	3.328	146.10
Kr	sphere	2.639	0.5542	0.03879	3.483	212.38
Xe	sphere	3.142	0.7854	0.06545	3.874	281.80
O_2	spherocylinder	4.420	0.4106	0.01000	2.958	168.00
CO	spherocylinder	4.800	0.8344	0.03963	3.225	145.35
CH_4	tetrahedron	3.405	0.6111	0.02470	3.535	194.00
C_2H_4	rectangle	8.800	3.480	0	2.950	383.00
C_2H_6	triangular prism	10.17	5.770	0.6530	2.840	444.00
C_3H_6	pentagon	10.51	5.260	0	3.439	475.00
C_3H_8	pentagon	12.75	7.750	0	3.310	515.14

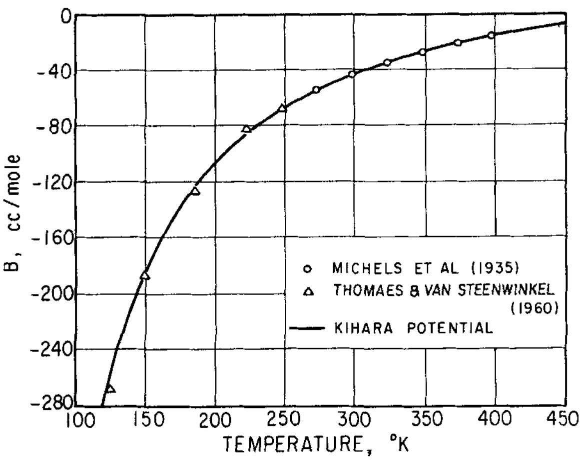

Fig. 4. Experimental and theoretical (Kihara) second virial coefficients for methane.

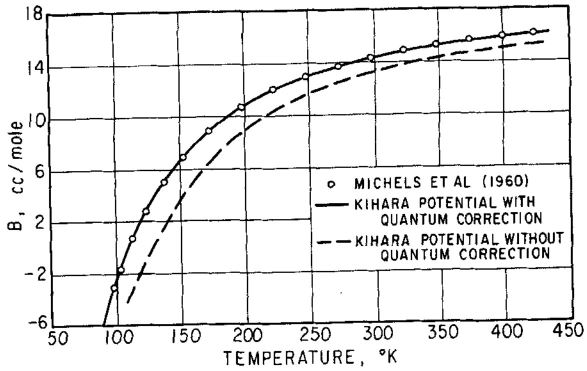

Fig. 5. Experimental and theoretical second virial coefficients for hydrogen.

in that case the Kihara parameters would be effective parameters which would not characterize the true potential. Such effective parameters cannot be used for making predictions of volumetric properties of mixtures or of pure components at low temperatures.

Equation (5) diverges at very low temperatures or small values of $(1/z)$. The lower temperature limit of applicability of Equation (5) depends on both Λ^* and the value of $(1/z)$. If it is assumed that this limit is given by the temperature at which the second term of Equation (5) becomes 25% of the first term, the following table gives the maximum value of Λ^* for various values of $(1/z)$:

$(1/z)$	$(\Lambda^*)_{max}$
6	3.3
4	2.6
2	1.37
1	1.05

With these results the lower temperature limits for the application of Equation (5) to the gases hydrogen, helium, and neon are 90°, 40°, and 45°K. respectively. At values of $(1/z)$ smaller than unity Equation (5) diverges regardless of the value of Λ^*.

Fluids with Significant Quadrupole Moments

The Kihara potential function considers only forces of repulsion due to overlapping of the electron clouds and forces of attraction due to fluctuating dipoles known as *London* or *dispersion forces*. In addition however there are intermolecular forces due to permanent quadrupole moments, and these are important for nitrogen, carbon dioxide, and acetylene. The quadrupole moments of these fluids are, respectively, 1.5, 3.0, and 3.0 × 10^{-26} esu-sq. cm. (*4*).

The second virial coefficient for these fluids is given by

$$B = B_{\text{Kihara}} + B_{\text{quadrupole}} \qquad (8)$$

It has been shown by Pople (*40*) that

$$B_{\text{quadrupole}} = -\frac{2}{3}\pi N \sigma^3 \left(\frac{7}{320}\right) Q^{*2} H_{10}(2\sqrt{z}) \qquad (9)$$

where

$$Q^* = \frac{Q^2}{U_o \sigma^5} \qquad (10)$$

The function H_{10} has been tabulated (*40*). Equation (9) strictly applies only as a correction for the Lennard-Jones potential. As an approximation it is assumed here that Equation (9) also applies as a suitable correction to the Kihara potential. The parameter σ is again given by Equation (7).

The second virial coefficients for substances possessing a significant quadrupole moment are computed by Equations (3), (7), (8), (9), and (10). The quadrupole correction depends on the parameters U_o, ρ_o, M_o, and the quadrupole moment of the molecule. As in the case of quantum corrections there are no additional unknown parameters; Equation (8) is fitted to the experimental data by the method previously described.

The resulting parameters are given in Table 4. Figure 6 gives a comparison of experimental and computed results for carbon dioxide and shows that quadrupole corrections are considerable in this case. The data for carbon dioxide could of course have been fitted without quadrupole corrections. But in that case the Kihara parameters would be effective parameters which would not characterize the true potential, and such effective parameters cannot be used to predict volumetric properties of mixtures or of pure components at low temperatures.

MIXTURES

Equation (1) applies for mixtures as well as for pure components. The second virial coefficient for a mixture, as derived from the principles of statistical mechanics, is

$$B_m(T) = \sum_i \sum_j y_i\, y_j\, B_{ij}(T) \qquad (11)$$

For example for a binary system of components 1 and 2 Equation (11) becomes

$$B_m = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (12)$$

where B_{11} and B_{22} are the second virial coefficients for the pure components

TABLE 3. KIHARA PARAMETERS FOR FLUIDS EXHIBITING QUANTUM EFFECTS

Substance	Core	M_o, A.	S_o, A.^{2}	V_o, A.^{3}	ρ_o, A.	U_o/k, °K.	Λ^*
He	none	0	0	0	2.921	9.927	2.670
H_2	rod	2.330	0	0	2.808	46.00	1.582
Ne	sphere	1.885	0.2827	0.01414	2.691	45.00	0.538

TABLE 4. KIHARA PARAMETERS FOR FLUIDS POSSESSING A SIGNIFICANT QUADRUPOLE MOMENT

Substance	Core	M_o, A.	S_o, A.^{2}	V_o, A.^{3}	ρ_o, A.	U_o/k, °K.	Q^*
N_2	spherocylinder	4.694	0.8130	0.03856	3.148	136.67	0.2110
CO_2	spherocylinder	9.173	2.469	0.1781	2.790	380.20	0.1793
C_2H_2	spherocylinder	10.47	7.581	1.701	2.925	401.80	0.1141

1 and 2, and B_{12} is the second virial coefficient for 1—2 interactions.

In general the interaction coefficient B_{ij} is given by the Kihara potential model (16) as

$$\frac{B_{ij}}{N} = \frac{2\pi}{3}\rho^3_{oij}F_3 + \frac{M_{oi}+M_{oj}}{2}\rho^2_{oij}F_2 + \left(\frac{S_{oi}+S_{oj}}{2} + \frac{M_{oi}M_{oj}}{4\pi}\right)\rho_{oij}F_1 + \frac{V_{oi}+V_{oj}}{2} + \frac{M_{oi}S_{oj}+M_{oj}S_{oi}}{8\pi} \tag{13}$$

where the F functions now depend on (U_{oij}/kT) but are the same functions as referred to in Equation (3). Of course Equation (13) reduces to Equation (3) in the case $i = j$.

In order to calculate B_{ij} the core parameters for the pure components, as well as for ρ_{oij} and U_{oij}, are required. The latter parameters, characterizing the potential function for interactions between unlike molecules, may be obtained from the pure component parameters from the semiempirical rule:

$$\rho_{oij} = \frac{1}{2}(\rho_{oi} + \rho_{oj}) \tag{14}$$

$$U_{oij} = \sqrt{U_{oi}U_{oj}} \tag{15}$$

Therefore with fluids requiring no quantum corrections and possessing negligible permanent electric moments Equations (13), (14), and (15) are used to calculate B_{ij} from the pure component parameters of molecules i and j.

To calculate B_{ij} for fluids requiring quantum corrections Equations (4) and (5) are used. However B_I^*, B_{II}^*, etc. are now functions of kT/U_{oij}, and the parameters Λ^* and σ become

$$\Lambda^*_{ij} = \frac{h}{\sigma_{ij}\sqrt{2\mu_{ij}U_{oij}}} \tag{16}$$

TABLE 5. VALUES OF Q^*_{ij} AND Λ^*_{ij} FOR SEVERAL MIXTURES

Mixture	Q^*_{ij}	Λ^*_{ij}
N_2-CO_2	0.1934	
He-H_2		2.112
He-Ne		1.389
H_2-Ne		1.215
He-A		0.888
He-N_2		0.886
He-O_2		0.864
H_2-A		0.797

TABLE 6. EXPERIMENTAL AND CALCULATED VALUES OF B_{12} AT 25°C.

Mixture	B_{12} [exp. (19)]	B_{12} (theor.)
N_2-H_2	+12.9	+11.4
N_2-CO_2	—41.7	—39.4
CO_2-H_2	—0.8	+0.7
He-A	+19.7	+14.8
C_2H_4-H_2	+3.1	+1.1
CO-N_2	—7.0	—6.9
CO-H_2	+12.8	+11.2
CO-CO_2	—42.9	—42.9

TABLE 7. EXPERIMENTAL AND CALCULATED VALUES OF B_m AT 30°C. FOR EQUIMOLAR MIXTURES

Mixture	B_m [exp. (7, 8)]	B_m (theor.)
CO_2-He	—16.1 ± 1.7	—18.3
CO_2-O_2	—52.0 ± 2.6	—54.0
CO_2-N_2	—51.5 ± 3.1	—49.9
CO_2-CO	—49.4 ± 2.3	—52.2
CO_2-H_2	—26.9 ± 1.9	—25.9

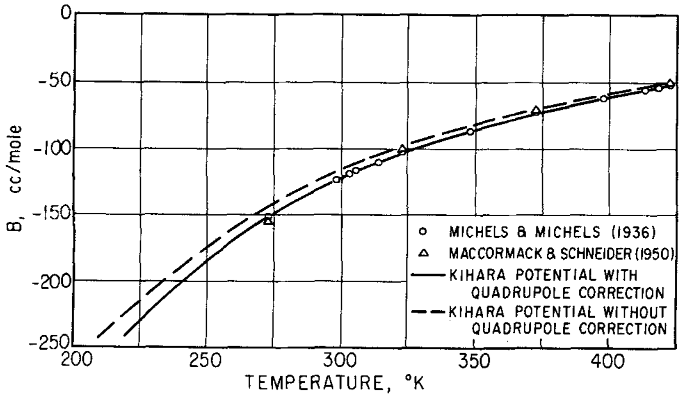

Fig. 6. Experimental and theoretical second virial coefficients for carbon dioxide.

$$\frac{1}{\mu_{ij}} = \left(\frac{1}{m_i} + \frac{1}{m_j}\right) \tag{17}$$

$$\sigma_{ij} = 2^{-1/6}\rho_{oij} + \frac{M_{oi}+M_{oj}}{4\pi} \tag{18}$$

At a given temperature the importance of the quantum correction can be judged from the magnitude of Λ^*_{ij}. For interactions between hydrogen and helium for example σ_{ij} and U_{oij} are small, and quantum corrections are large. However for interactions between one quantum fluid, such as hydrogen, and a nonquantum fluid, such as argon, the value of Λ^*_{ij} may still be large enough to require a quantum correction; the magnitude of the correction will increase as the temperature decreases. Thus quantum corrections must be considered even if only one of the fluids is a quantum gas (hydrogen, helium, or neon). Values of Λ^*_{ij} for several such mixtures are given in Table 5.

Equations (8) and (9) are used to calculate B_{ij} for fluids requiring quadrupole corrections. H_{10} is now a function of $\left[2\sqrt{\frac{U_{oij}}{kT}}\right]$; the parameter Q^* is now

$$Q^*_{ij} = \frac{Q_i Q_j}{U_{oij}\sigma_{ij}^5} \tag{19}$$

and σ_{ij} is again given by Equation (18). Equation (19) actually applies to molecules possessing quadrupole moments of like sign. The forces between quadrupole moments of unlike sign are somewhat greater than those of like sign. However the sign (+ or —) of the molecular quadrupole is seldom known (*4*), and Equation (19) seems justified until further data are available. A value for Q^*_{ij} for one such quadrupole-quadrupole mixture is given in Table 5.

Equation (19) shows that quadrupole corrections need be considered only for interactions between the fluids acetylene, carbon dioxide, and nitrogen; if one of the fluids in a binary mixture has zero quadrupole moment, the value of Q^*_{ij} vanishes. It is assumed here that quadrupole-induced quadrupole forces are negligible.

In summary to calculate B_{ij} for components i and j Equations (13), (14), and (15) are used to calculate $[B_{\text{Kihara}}]_{ij}$. If quantum corrections are required, Equations (5), (16), (17), and (18) are used to determine the quantum correction $[B_{\text{quantum}}]_{ij}$. If quadrupole corrections are required, Equations (9), (18), and (19) give the magnitude of the quadrupole correction $[B_{\text{quadrupole}}]_{ij}$.

COMPARISON WITH DATA

Reliable data for second virial coefficients of mixtures at normal temperatures are not plentiful, and data at low temperatures are very scarce. Table 6 compares calculated values of B_{12} with those observed by Michels and Boerboom (*19*) at 25°C., and Table 7 compares calculated values of B_m with those observed by Cottrell (*7*, *8*). The agreement is very good; deviations are essentially no larger than the probable experimental uncertainty.

It should be noted that the experimental values of B_{12} shown in Table 6 were obtained from

$$B_{12} = \frac{v_e}{2y_1 y_2}\left(\frac{\Delta PV}{PV}\right) + \frac{1}{2}(B_{11} + B_{22}) \qquad (20)$$

Michels and Boerboom record the experimental value of $\left(\frac{\Delta PV}{PV}\right)$; v_e is the ideal gas molar volume at 25°C. and 1 atm. The pure component virial coefficients B_{11} and B_{22} used to obtain the experimental B_{12} values recorded in Table 6 are the same as the values given in reference *19*.

Table 8 compares calculated and experimental values of B_{12} for mixtures at 90°K.; the data are taken from the work of Knobler et al. (*17*). The values of B_{12} obtained by these workers were not measured directly but were calculated from

$$B_{12} = \frac{1}{2}(B_{11} + B_{22}) + E \qquad (21)$$

where B_{11} and B_{22} are the second virial coefficients of the pure components, and the quantity E is related to the pressure change observed in the mixing of the pure gases. B_{11} and B_{22} were not measured by these workers but were obtained from other experimental data in the case of helium, hydrogen, and neon, and were calculated with the Lennard-Jones parameters tabulated in reference *12* in the case of nitrogen, oxygen, and argon. A comparison of the values used by Knobler et al. for the second virial coefficients of the pure components and the values calculated by means of the methods of this paper is given in Table 9. These revised values of B_{11} and B_{22} were used to recalculate the values of B_{12} given by Knobler et al. The experimental values of B_{12} given in Table 8 are the recalculated quantities.

The agreement between experimental and calculated values of B_{12} in Table 8 is good, although the deviations for oxygen-containing systems appear to be just a little larger than the probable experimental uncertainty. It has been known for some time that the properties of oxygen deviate slightly from those exhibited by other cryogenic fluids (42). It is probable that such deviations are related to the paramagnetic character of oxygen, but it is difficult at this time to make a quantitative estimate of this effect.

TABLE 8. EXPERIMENTAL AND CALCULATED VALUES OF B_{12} AT 90°K.

Mixture	B_{12}[exp. (17)]	B_{12} (theor.)
He-H_2	+13.0	+8.5
He-Ne	+4.6	+6.5
He-N_2	+1.4	−2.6
He-O_2	−19.2	−6.3
He-A	+0.4	−6.6
Ne-H_2	−5.2	−7.2
Ne-N_2	−45.6	−48.8
Ne-O_2	−58.6	−54.8
Ne-A	−45.1	−55.1
N_2-O_2	−235.7	−213.7
N_2-A	−213.0	−206.9
A-H_2	−58.9	−54.3
A-O_2	−238.8	−230.0

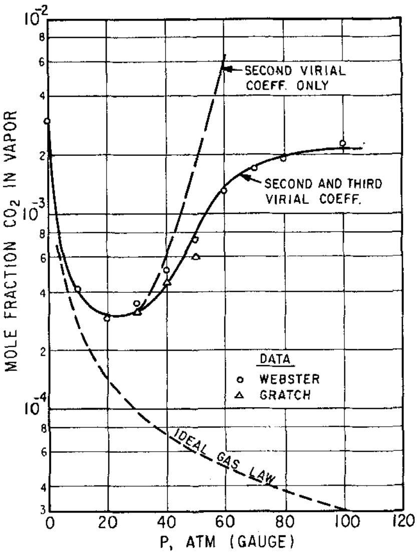

Fig. 7. Solubility of solid carbon dioxide in air at 143°K.

The results given in Tables 6, 7, and 8 support the validity of the semiempirical mixing rules given by Equations (14) and (15). However it has been observed previously (*41*) that in mixtures containing one component having small molecules and other component having large molecules the geometric mean given by Equation (15) is slightly large, as is suggested by the London theory of dispersion forces. In such systems therefore there may be a tendency for the calculated virial coefficient B_{12} to be slightly lower (algebraically) than the true value. However this error is never large in the case of calculations based on the Kihara potential. Additional experimental data will be needed to decide whether a refinement in the mixing rules [Equations (14) and (15)] is needed.

The experimental results of Fender and Halsey (*11a*) for the second virial coefficients of argon, krypton, and argon-krypton mixtures in the temperature range 80° to 140°K. were published after the parameters of the Kihara potential had been evaluated. When these experimental results are compared with second virial coefficients as calculated by the methods described in this paper, excellent agreement is obtained. The average error between the eleven experimental points for pure argon and the predicted values is 1.7 cc./mole; for the eleven experimental points for pure krypton the average error is 2.3 cc./mole. This agreement at low temperatures is particularly satisfying because the experimental data which were used to calculate the Kihara parameters were obtained at substantially higher temperatures, as shown in Table 1. The agreement for mixtures is nearly as good as for the pure gases; the average error between the predicted values of B_{12} for argon-krypton mixtures and the nine experimental points of Fender and Halsey is 4.3 cc./mole. This error is about 2% and is within the probable experimental error. These favorable comparisons therefore give additional confidence to the predictions of low temperature properties based on the Kihara potential.

APPLICATION TO PHASE EQUILIBRIA

Virial coefficients are useful for calculating the fugacity of a component in a compressed gas mixture. It has been shown previously (*41*) that the fugacity coefficient is given by

$$\ln \phi_i = \frac{2}{v_m}\sum_j y_j B_{ij} + \frac{3}{2}\frac{1}{v_m^2}\sum_j \sum_k y_j y_k C_{ijk} + \ldots - \ln Z_m \qquad (22)$$

In phase equilibrium the fugacity of a component i is the same in all phases; Equation (22) enables calculation of the fugacity of component i in the gas phase provided the various virial coefficients are known. At very low densities $\phi_i \to 1$, and at moderate densities the terms in $\frac{1}{v_m^2}$ may be considered negligible compared with those in $\frac{1}{v_m}$. At moderate densities therefore third virial coefficients may be neglected.

To illustrate the use of Equation (22) consider the solubility of solid carbon dioxide in compressed air at 143°K. The fugacity of solid carbon dioxide is readily computed from the vapor pressure and density of the

TABLE 9. SECOND VIRIAL COEFFICIENTS OF PURE GASES AT 90°K.
B, CC./MOLE

Gas	Values calc. by Knobler et al. (*17*)	Values calc. by this paper
He	+10.8	+11.6
H_2	−5.17	−5.5
Ne	−2.08	−8.4
N_2	−180.	−202.8
O_2	−208.	−238.5
A	−209.	−222.2

solid. The fugacity of carbon dioxide in the gas phase is computed from Equation (22), and the volume and compressibility factor of the gas mixture are calculated from the virial equation. The techniques described here are used to calculate the second virial coefficients. Since Equation (22) is a converging series in $(1/v)$, the various C terms are not as important as the various B terms; in fact they may be neglected at moderate densities. At higher densities however the C terms are not negligible. Unfortunately only approximate techniques are available for use in calculating third virial coefficients. The third virial coefficients for the pure components were calculated by statistical formulas with the Lennard-Jones potential (*12*), while the third virial cross coefficients were estimated by a technique described by Sutton (*44*). Figure 7 shows the results. The lower dashed line illustrates the solubilities obtained when all virial coefficients are neglected, and the upper dashed line shows the solubilities obtained when only second virial coefficients are used. The solubilities obtained when second and third virial coefficients are used are seen in the continuous line. These calculated results are compared with the experimental solubility data of Webster (*47*) [and also of Gratch (*47*)]. Figure 7 shows that the ideal gas calculation leads to large errors. Calculations based on the virial equation with only second virial coefficients are reliable up to about 40 atm., and calculations employing second and third virial coefficients are good up to at least 100 atm.

In this example the third virial coefficient becomes important at a rather low pressure because the operating temperature is not far removed from the critical temperature of the gas. If hydrogen instead of air had been the gas at this temperature, third virial coefficients could have been neglected in the calculation up to pressures of at least 100 atm.

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NOTATION

B = second virial coefficient
B_0^*, B_I^*, B_{II}^* = function of $(1/z)$
C = third virial coefficient
E = excess quantity, Equation (21)
f = fugacity
F = function of z
h = Planck's constant
H_{10} = function of $2\sqrt{z}$
k = Boltzman's constant
m = mass of atom or molecule
M_0 = parameter of Kihara core
N = Avogadro's number
P = pressure
Q = molecular quadrupole moment
Q^* = reduced quadrupole moment (dimensionless)
R = gas constant
S_0 = surface parameter of Kihara core
v = molar volume
V_0 = volume parameter of Kihara core
T = absolute temperature
U = potential energy
U_0 = maximum (negative) potential energy
y = mole fraction in vapor phase
z = U_0/kT
Z = compressibility factor

Greek Letters

Λ^* = quantum mechanical parameter (dimensionless)
ρ = shortest distance between molecular cores
ρ_0 = shortest distance between molecular cores at energy minimum
σ = separation of molecular centers at zero potential energy
μ = reduced mass
ϕ = fugacity coefficient = f/yP

Subscripts

m = mixture
i, j, k = components

LITERATURE CITED

1. Beattie, J. A., R. J. Barriault, and J. S. Brierley, *J. Chem. Phys.*, **19**, 1222 (1951).
2. Beattie, J. A., J. S. Brierley, and R. J. Barriault, *ibid.*, **20**, 1615 (1952).
3. Bowen, H. J. M., et al., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc., London, England (1958).
4. Buckingham, A. D., *Quart. Revs. (London)*, **13**, 183 (1959).
5. Connolly, J. F., and G. A. Kandalic, *Phys. Fluids*, **3**, 463 (1960); Doc. No. 6307, Documentation Institute, Library of Congress, Washington, D.C.
6. Cook, D., *Can. J. Chem.*, **35**, 268 (1957).
7. Cottrell, T. L., and R. A. Hamilton, *Trans. Faraday Soc.*, **52**, 156 (1956).
8. ———, and R. P. Taubinger, *ibid.*, p. 1310.
9. Crommelin, C. A., J. Palacios Martinez, and H. Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 154a (1919).
10. Danon, F., and K. S. Pitzer, *J. Chem. Phys.*, **36**, 425 (1962).
11. De Boer, J., and A. Michels, *Physica*, **5**, 945 (1938).

11a. Fender, B. E. F., and G. D. Halsey, Jr., *J. Chem. Phys.*, **36**, 1881 (1962).

12. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
13. Holborn, L., and J. Otto, *Z. Physik*, **33**, 1 (1925).
14. Johnston, H. L., et al., "American Institute of Physics Handbook," Chap. 4, McGraw-Hill, New York (1957).
15. Kihara, Taro, *Revs. Modern Phys.*, **25**, 831 (1953).
16. *Ibid.*, **27**, 412 (1955).
17. Knobler, C. M., J. J. M. Beenakker, and H. F. P. Knapp, *Physica*, **25**, 909 (1959).
18. MacCormack, K. E., and W. G. Schneider, *J. Chem. Phys.*, **18**, 1269 (1950).
19. Michels, A., and A. J. H. Boerboom, *Bull. Soc. Chim. Belg.*, **62**, 119 (1953).
20. Michels, A., W. De Graaff, and C. A. Ten Seldam, *Physica*, **26**, 393 (1960).
21. Michels, A., and M. Geldermans, *ibid.*, **9**, 967 (1942).
22. Michels, A., J. M. Levelt, and W. De Graaff, *ibid.*, **24**, 659 (1958).
23. Michels, A., J. M. Lupton, T. Wassenaar, and W. De Graaff, *ibid.*, **18**, 121 (1952).
24. Michels, A., and C. Michels, *Proc. Roy. Soc. (London)*, **A153**, 201 (1936).
25. Michels, A., and G. W. Nederbragt, *Physica*, **2**, 1000 (1935).
26. Michels, A., H. W. Schamp, and W. De Graaff, *ibid.*, **20**, 1209 (1954).
27. Michels, A., W. Van Straaten, and J. Dawson, *ibid.*, **20**, p. 17.
28. Michels, A., T. Wassenaar, and P. Louwerse, *ibid.*, p. 99.
29. ————, *ibid.*, **26**, 539 (1960).
30. ————, R. J. Lunbeck, and G. J. Wolkers, *ibid.*, **19**, 287 (1953).
31. Michels, A., Hub Wijker, and H. K. Wijker, *ibid.*, **15**, 627 (1949).
32. Michels, A., and H. Wouters, *ibid.*, **8**, 923 (1941).
33. ———— and J. De Boer, *ibid.*, **1**, 587 (1934).
34. Myers, A. L., and J. M. Prausnitz, *Physica*, **28**, 303 (1962).
35. Nijhoff, G. P., and W. H. Keesom, *Comm. Phys. Lab. Univ. Leiden*, No. 179b (1925).
36. Onnes, H. Kamerlingh, and C. Braak, *ibid.*, No. 100a (1907).
37. Onnes, H. Kamerlingh, and C. A. Crommelin, *ibid.*, No. 128 (1912).
38. Otto, J., A. Michels, and H. Wouters, *Physik. Z.*, **35**, 97 (1934).
39. Pitzer, K. S., and R. F. Curl, Jr., *J. Am. Chem. Soc.*, **79**, 2369 (1957).
40. Pople, J. A., *Proc. Roy. Soc. (London)*, **A221**, 508 (1954).
41. Prausnitz, J. M., and R. N. Keeler, *A.I.Ch.E. Journal*, **7**, 399 (1961).
42. Rowlinson, J. S., "Liquids and Liquid Mixtures," Chap. 8, Butterworths Scientific Pub., London, England (1959).
43. Schafer, Klaus, *Z. Phys. Chem.*, **B36**, 85 (1937).
44. Sutton, J. R., thesis, Univ. of Manchester, Manchester, England (1955).
45. Thomaes, G., and R. Van Steenwinkel, *Nature*, **187**, 229 (1960).
46. van Urk, A. Th., *Comm. Phys. Lab. Univ. Leiden*, No. 169e (1924).
47. Webster, T. J., *Proc. Roy. Soc. (London)*, **A214**, 61 (1952).
48. Whalley, E., Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **33**, 633 (1955).
49. White, David, Thor Rubin, Paul Camky, and H. L. Johnston, *J. Phys. Chem.*, **64**, 1607 (1960).

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