$u$ = drop velocity, cm./sec.
$v_s$ = local velocity at surface of drop, cm./sec.

**Greek Letters**

$\alpha$ = velocity potential for irrotational flow around sphere, cm$^4$/sec.
$\beta$ = stream function for irrotational flow around sphere cc./sec.
$\gamma$ = defined in discussion after Equation (1)
$\eta$ = defined in discussion after Equation (1)
$\theta$ = polar angle measured from rear stagnation point
$\mu$ = viscosity, poises
$\nu$ = kinematic viscosity, stokes
$\rho$ = continuous phase density, g./cc.
$\rho_d$ = dispersed phase density, g./cc.
$\sigma$ = interfacial tension, dynes/cm. or g./sec.$^2$
$\Psi$ = stream function for boundary layer flow around sphere written in terms of the coordinates $\alpha$ and $\beta$

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# Application of the Kihara Potential to High Pressure Phase Equilibria

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**This paper is concerned with the virial equation of state as applied to vapor mixtures at moderate densities. The required virial coefficients for small molecules can usually be estimated from generalized corresponding states correlations, but these correlations are not sufficient for mixtures which contain one very heavy and one very light component. It is shown that for such mixtures the necessary virial coefficients can be calculated by statistical thermodynamics with a potential function proposed by Kihara. This type of calculation is especially useful at low temperatures where virial coefficients have not been measured because of large experimental difficulties. Application of the Kihara potential is demonstrated with the computation of K values for heavy components for several mixtures at advanced pressures; good agreement with experimental results is obtained.**

**The virial equation may in some cases be used to test data for thermodynamic consistency, and for illustration it is shown that recently reported K data for propane in compressed hydrogen are thermodynamically inconsistent and too large by about two orders of magnitude.**

Experimental studies in high-pressure fluid-phase equilibria are numerous and have appeared in the technical literature for many years. However very little effort appears to have been expended on the application of theoretical concepts to the problem of testing, correlating, and eventually predicting high-pressure phase-equilibrium relationships. This is unfortunate, primarily for two reasons. First, it is inconceivable that complete experimental data will ever become available for the almost infinite number of binary and multicomponent systems which are composed of the various gases and liquids of technical interest today, not to mention the even larger number of such fluids which may be of interest in the future. As a result it becomes necessary to carefully obtain data for a few representative systems and then to interpret these data with as much physical insight as possible. Such interpretation, to be most useful, must be guided by theoretical concepts not only because such concepts help to understand what intermolecular forces are responsible for the observed phase behavior but also because an interpretation or correlation based only on empirical grounds cannot be successful when data are available for only a very limited number of systems.

Second, the application of theoretical methods enables the experimentalist to test his results for internal and thermodynamic consistency. At present such testing is almost never done by experimentalists in the high-pressure field, and consequently inaccurate data have been reported and have been uncritically accepted by the scientific and engineering community. As a result empirical correlations based on faulty data extend the error by producing incorrect predictions for systems for which no data are as yet available. Occasionally a sound correlation scheme may fail correctly to predict the apparent behavior of a given system, and the scheme is therefore rejected, due not to any fault in the correlation method but rather to the gross inaccuracy of the experimental data. An example of such a case is given towards the end of this paper.

Theoretical methods in high pressure phase equilibria are still in an early stage of development. However in a few cases of technical interest the results of modern molecular physics are applicable to the problem of high-pressure behavior. This paper discusses the application of the virial equation to the testing, correlation, and prediction of K values and shows how the required virial coefficients can be obtained with the help of the Kihara potential.

## THE VIRIAL EQUATION

The derivation of the virial equation, its limitations, and its theoretical significance have been amply discussed previously (*9, 17, 20*). It is sufficient to recall that the great advantage of the virial equation for mixtures lies in its ability to predict precisely the composition dependence of the constants which appear in the equation; its great disadvantage lies in its restriction to moderate densities. In many cases of technical interest however the advantage is much more important than the disadvantage; this is especially true in equilibria where the light component, in excess in the vapor phase, is at a temperature far above its critical temperature, for under these conditions the virial equation is valid up to very high pressures. For example in a case where the vapor phase consists primarily of hydrogen, the virial equation is useful up to pressures of several thousand pounds per square inch.

Consider now the phase behavior of a heavy component $i$ in a given mixture at a certain temperature and pressure. The K value for such a component is given exactly by

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^L}{\phi_i P} \qquad (1)$$

It is the vapor phase fugacity coefficient $\phi_i$ which is related to the virial equation. If the virial equation is written in the proper form

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \ldots . \qquad (2)$$

where $z$, $B$, $C$, and $v$ all refer to the mixture of $n$ components, then the fugacity coefficient is given exactly by

$$\ln \phi_i = \frac{2}{v} \sum_{j=1}^{n} y_j B_{ij} + \frac{3}{2v^2} \sum_{j=1}^{n} \sum_{k=1}^{n} y_j y_k C_{ijk} + \ldots - \ln z \qquad (3)$$

Equation (3) involves no arbitrary assumptions but follows directly from the statistical mechanical derivation of the virial equation.

The ability of the virial equation to give a good representation of the volumetric behavior of gases and gas mixtures over a limited (but useful) density range has not been sufficiently appreciated and therefore a few illustrations will be given. For example volumetric data for ethane, propane, and pentane have been examined by David and Hamann (*5*), and their results are shown in Figure 1. The lines are plots of the virial equation whose second and third virial coefficients were obtained from the data, and it is seen that the virial equation terminated after the third virial coefficient gives very good representation of the data for the moderate density region.

For mixtures Figure 2 shows a graphical determination of the second and third virial coefficients from volumetric data for two systems (*21, 22*). On this plot the second virial coefficient is obtained from the intercept and the third virial coefficient from the slope. The data for nitrogen-ethane appear to be highly consistent, but the low-density results for the methane-decane system appear to be slightly in error. At high densities of course there is large deviation from straight-line behavior, since the virial equation terminated after the third coefficient is no longer adequate. Figure 3 shows the compressibility factors for these systems as a function of reduced density, and again it is seen that the virial equation gives a good representation of the volumetric behavior. Finally Figure 4 shows the compressibility factor for the butane-carbon dioxide system (*15*). In this case the dotted lines were computed with the virial equation, first with only the second virial coefficient and then with the second and third coefficients; in these calculations the coefficients were obtained from reliable generalized correlations which are briefly described in the next section and which are independent of this particular set of volumetric data. Figure 4 shows that the virial equation terminated after the second coefficient gives a good representation of the data up to a reduced density of almost 0.5; the predicted results with the second and third virial coefficients appear to be reasonably good up to even higher densities. Without further analysis it would be impossible to say whether the small disagreement between computed and observed results for this system is due to inadequacies of the generalized correlation or else due to inaccuracies in the experimental data. In any case it is clear from these illustrations that the virial equation can, to a good approximation, represent the volumetric behavior of gases and gas mixtures for a certain density range and that in view of the theoretical rigor of this equation it is extremely useful for computing fugacities of components in gaseous mixtures.

## PREDICTION OF VIRIAL COEFFICIENTS

Various attempts have been made to present generalized correlations for the second virial coefficients, and a few such attempts were directed at the third virial coefficients. These correlations are all based in some way on the theorem of corresponding states, and in recent years it has been possible to extend them to certain types of mixtures (*5, 7, 8, 18, 20, 24*). However one of the difficulties in applying corresponding-states ideas to the correlation of virial coefficients is due to the fact that two parameters (a characteristic temperature and a characteristic volume) are insufficient to give an adequate representation of the data, especially at lower temperatures. This insufficiency is illustrated by the behavior of the second virial coefficients of the normal paraffins which were plotted by McGlashan and Potter (*12*) on reduced coordinates as shown in Figure 5. The lines for the different hydrocarbons tend to coincide at the higher reduced temperatures but diverge noticeably at lower temperatures; in general the reduced virial coefficients tend to decrease (algebraically) as the molecular weight increases. From these as well as other data it became obvious that two characteristic parameters are insufficient and that a third parameter would be required if second virial coefficients were to be successfully correlated. Acordingly, Pitzer and Curl (16) proposed a generalized equation for the second virial coefficient which in addition to two critical properties introduces a third parameter called the *acentric factor;* this equation predicts the second virial coefficients of pure nonpolar gases with very high accuracy down to a reduced temperature of 0.5. While the equation of Pitzer and Curl is an important contribution to the thermodynamics of high pressure phase equilibria, it leaves unanswered two important questions related to the calculation of second virial coefficients as required in typical phase equilibrium problems. First, their equation was derived for pure components only, and hence it cannot by itself predict virial coefficients for mixtures. In the past few years an effort has been made (*17, 18*) on the basis of the theory of intermolecular forces to extend the Pitzer and Curl equation to mixtures, and the results which were obtained have been quite satisfactory; however the semiempirical methods used in this extension should, if possible, be replaced by a procedure which is more satisfactory theoretically. Second, the Pitzer and Curl equation is basically empirical, and since experimental data on virial coefficients are not available at low reduced temperatures because of very large experimental difficulties, the Pitzer and Curl equation

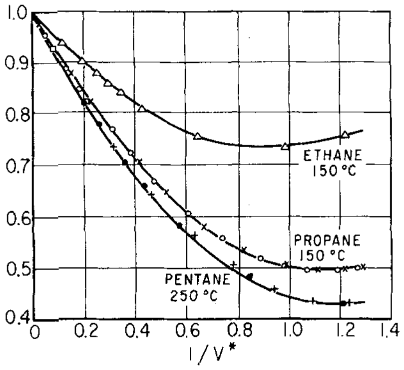

**Fig. 1. A comparison of some experimental and fitted isotherms for pure components (Hamann).**

cannot be reliably extrapolated to reduced temperatures less than 0.5. This latter limitation is frequently not important, but in some low-temperature problems the fugacity coefficient of a heavy component will depend slightly on its second virial coefficient; hence it is sometimes important to compute this coefficient at a reduced temperature less than 0.5, if for no other reason than to ascertain whether or not it can be neglected in Equation (3). One possible method for computing second virial coefficients at low temperatures is to use the results obtained from the Lennard-Jones potential which can be used for any desired temperatures. However this predicts virial coefficients in terms of only two characteristic parameters, and hence it is not adequate for molecules other than very simple ones, especially at low temperatures where the effect of a third characteristic parameter becomes increasingly important.

While the Pitzer and Curl correlation is certainly very useful, the two limitations mentioned above suggest the desirability of considering some alternate technique for computing virial coefficients of gas mixtures containing complex molecules and for computing virial coefficients of heavy components at very low reduced temperatures. Such a technique is provided by the Kihara potential which is described below.

In what has been said above and in what is to follow, primary attention has been given to the second rather than the third virial coefficient. This is because much more is known experimentally about the second virial coefficient and because theoretical calculations for the second are much easier than those for the third virial coefficient. Techniques for predicting the third virial coefficient of gas mixtures are still quite crude, but fortunately for practical application the contributions to the fugacity coefficient $\phi$ of terms involving $C$ are almost always less important than those involving $B$. In fact in many cases of practical interest the terms involving $C$ can be neglected entirely.

The next two sections discuss the application of the Kihara potential to the calculation of the second virial coefficient. In principle the Kihara potential could be used also to compute third (or even higher) virial coefficients. However the very extensive statistical mechanical calculations required to achieve this goal have not as yet been performed.

## THE KIHARA POTENTIAL FOR PURE GASES

The virial coefficients of a gas are directly related to the potential energy function which describes the relation of the potential energy between two (or more) molecules as a function of the distance between them and, in the case of more complicated molecules, of their relative orientations. For example for simple molecules the second virial coefficient depends on the potential energy in accordance with

$$B(T) = 2N\pi \int_0^\infty \left[1 - \exp\frac{-U(r)}{kT}\right] r^2\,dr \quad (4)$$

Probably the best known potential function is that of Lennard-Jones, who considers molecules to be soft spheres which differ from hard spheres in the sense that soft spheres can interpenetrate at high enough energies, whereas hard spheres cannot. Kihara has extended the Lennard-Jones model in two ways. First he considers each soft molecule to have an impenetrable central region which is called the *core*. Secondly he recognizes that molecular shapes may be far removed from those corresponding to a sphere and correspondingly he permits wide latitude in his model in assigning appropriate molecular shape to a particular case. The geometry of the core is chosen in keeping with the known shape of the molecule; the numerical parameters which are used in the quantitative description of the core are determined only by bond angles and bond lengths or by similar fundamental data on the size and shape of the molecule.

A few core models for some common molecules are shown in Figures 6, 7, and 8. The models shown for nitrogen and methane have been proposed by Kihara (*10*), and those for normal paraffins and benzene are due to Connolly and Kandalic (*4*). The dumbbell model is proposed here to apply to molecules of very irregular shape.

In the Kihara model each core is now surrounded by a penetrable (soft) shell which has a thickness $\rho_0$. The potential energy between two molecules can then be written

$$U(\rho) = U_0\left[\left(\frac{\rho_0}{\rho}\right)^{12} - 2\left(\frac{\rho_0}{\rho}\right)^{6}\right] \quad (5)$$

where the independent variable $\rho$ is not the distance between molecular centers (as it is in the Lennard-Jones potential) but it is the distance between the surface of the impenetrable core of one molecule to that of the other.

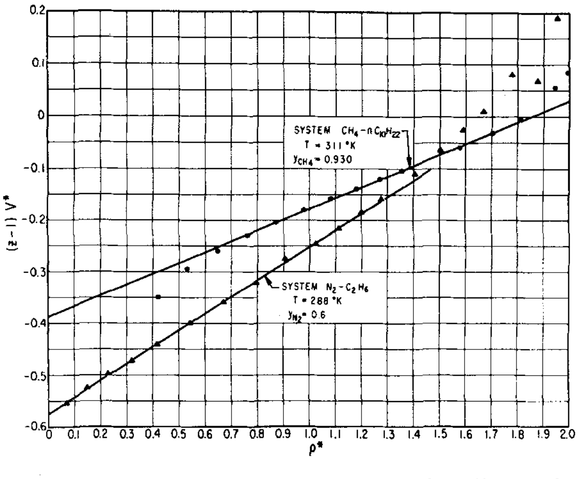

**Fig. 2. Determination of second and third virial coefficients for mixtures**

$$V^* = \frac{V_{\mathrm{mix}}}{\Sigma\, x_i V_{ci}} \qquad \rho^* = \frac{1}{V^*}.$$

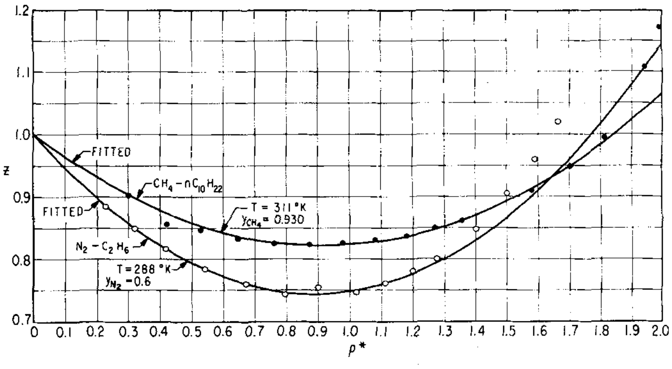

**Fig. 3. Experimental and fitted isotherms for two binary systems.**

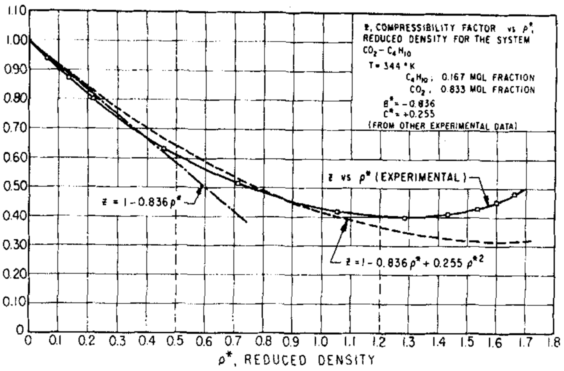

Fig. 4. Convergence of the virial equation.

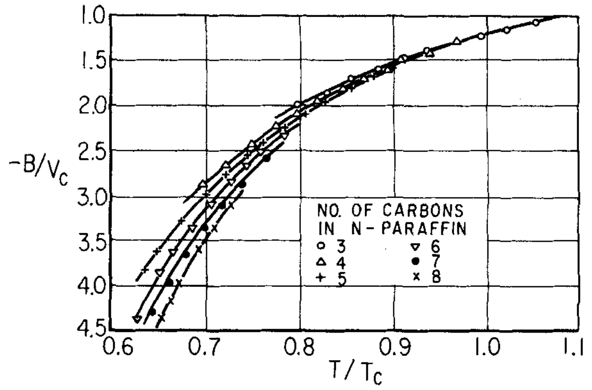

Fig. 5. The reduced second virial coefficient $B/V_c$ plotted against reduced temperature $T/T_c$ (McGlashan and Potter).

It is clear that the distance between core surfaces will depend on the mutual orientation of the two molecules. Kihara arbitrarily fixes the orientation of both interacting molecules; then he allows one molecular core to move over all points of the surface of the second molecular core which remains in a fixed orientation. Next he considers the second molecular core in all possible orientations. Finally, by the use of some topological and averaging theorems (*10*), Kihara arrives at the result for the second virial coefficient of a pure component:

$$B = \frac{2\pi}{3}\rho_0^3 F_3 + M_0\rho_0^2 F_2 + \left(S_0 + \frac{1}{4\pi}M_0^2\right)\rho_0 F_1 + \left(V_0 + \frac{1}{4\pi}M_0 S_0\right) \quad (6)$$

In this expression $M_0$ is the surface integral of mean curvature of the core over the core surface and is given for smooth curved surfaces by

$$M_0 = \int_s \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) ds \quad (7)$$

with $R_1$, $R_2$ principal radii of curvature. For polygonal or polyhedral cores $M_0$ is given by

$$M_0 = \frac{1}{2}\sum_{m=1}(\pi - \alpha_m)\, l_m \quad (8)$$

with $\alpha_m$ the dihedral angle of the mth edge, and $l_m$ is the length of the mth edge. The functions $F_1$, $F_2$, and $F_3$ are functions of $U_0/kT$ and have been tabulated by Kihara and extended by Connolly (*4*). The function $F_3$ is proportional to the Lennard-Jones function for spherical molecules. When the core degenerates to a point, $S_0$, $V_0$, and $M_0$ are equal to zero and the Kihara expression becomes identical to the Lennard-Jones expression for the second virial coefficient.

In deriving his result it was necessary for Kihara to impose the restriction that the molecular core be convex; otherwise some of the topological theorems would not be applicable.

For molecules of simple geometric shape it is easy to devise a convex core for use with the Kihara model. For instance the impenetrable core for the methane molecule may be constructed by connecting the midpoints of the four hydrogen atoms, thus forming a tetrahedron. Similarly Connolly has shown how a rectangle may be used as the core for normal alkanes with considerable success. In the case of a molecule such as 2,2,4-trimethyl pentane such simple concepts cannot be used; it is necessary to consider what a molecule actually sees. An approaching molecule would see 2,2,4-trimethyl pentane as two molecular fragments, isobutyl and isopropyl radicals, connected by a single carbon atom. Now associate with each carbon atom in the fragments a volume equal to that of the methane core of Kihara, sum the volumes, and consider these volumes to be those of two spherical equivalent molecular fragments; this yields radii of spheres whose centers are separated by the distance between the terminal carbon atoms in a $\overset{C\quad C}{\overset{\diagdown\;\diagup}{C}}$ bond. The result is a core of a dumbbell shape, and in order for this core to be convex the spheres must be connected by a tangent enveloping conic surface, as shown in Fig. 8. Appropriate formulas have been developing for obtaining $S_0$, $V_0$, and $M_0$ for this core model. The second virial coefficient for 2,2,4-trimethyl pentane has been closely fitted to the empirical equation of Pitzer and Curl by the use of the dumbbell core.

In order to obtain the Kihara parameters $\rho_0$ and $U_0$ it is necessary first to choose the appropriate core parameters for the molecule under consideration. Then two plots are prepared: $B/l^3$ vs. log $T$ with the experimental data, with $l$ some appropriate core parameter, and $B/l^3$ vs. log $kT/U_0$, with $\rho_0$ as the parameter. The second plot is superimposed on the first and shifted until the desired fit is obtained for a certain value of $\rho_0$. Then the abscissas are compared and $U_0/k$ is obtained. The suitable constants, $U_0/k$ and $\rho_0$, and the core parameters, once determined, may of course be stored in an electronic computer subroutine and applied to phase-equilibrium problems in adsorption, fractional distillation, etc. By fitting limited available volumetric data to the Kihara model it is possible to predict volumetric behavior over a large temperature range. A set of parameters for some of the molecules indicated by Figures 6, 7, and 8 is given in Table 1.

TABLE 1. PARAMETERS FOR KIHARA MODEL

| Substance | $l$, Å. | $V_0$, Å³. | $S_0$, Å.² | $M_0$, Å. | $\rho_0$, Å. | $U_0/k$, °K. |
|---|---|---|---|---|---|---|
| $N_2$ | $l_1 = 1.094$ | 0 | 0 | 3.44 | 3.47 | 124 |
| $CH_4$ | $l_1 = 1.785$ | 0.67 | 5.52 | 10.23 | 1.92 | 378 |
| $C_6H_6$ | $l_1 = 1.39$ | 0 | 10.14 | 13.2 | 3.4 | 850 |
| $C_5H_{12}$ | $l_1 = 1$<br>$l_2 = 4.68$ | 0 | 9.36 | 17.8 | 2.7 | 900 |
| $C_{10}H_{22}$ | $l_1 = 1$ | 0 | 21.06 | 36.2 | 2.7 | 1,276 |
| i-$C_8H_{18}$ | $l_1 = 0.861$<br>$l_2 = 0.783$<br>$l_3 = 2.8$ | 4.483 | 48.80 | 18.97 | 2.5 | 1,176 |

## THE KIHARA POTENTIAL FOR GAS MIXTURES

The second virial coefficient of a mixture is given by

$$B(\text{mix}) = \sum_i \sum_j y_i y_j B_{ij} \quad (9)$$

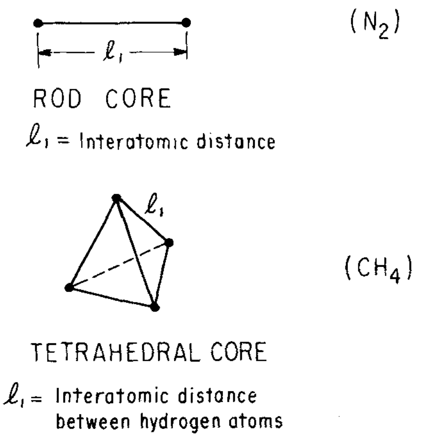

Fig. 6. Models of simple polyatomic molecules.

The various $B$ terms on the right-hand side consist of two types, one where $i$ and $j$ are the same and the second where $i$ and $j$ are different. The first type of course reflects the interactions between two similar molecules and therefore refers to the pure components in the mixture. The second type however represents the interaction between dissimilar molecules, and this is characteristic of the mixture. For the case where $i \neq j$ Kihara has shown (*11*) that his model may be used to obtain the expression

$$B_{ij} = \frac{2\pi}{3}\rho^3_{0ij} F_3 + \frac{M_{0i} + M_{0j}}{2}\rho^2_{0ij} F_2 + \left(\frac{S_{0i} + S_{0j}}{2} + \frac{M_{0i} M_{0j}}{4\pi}\right)\rho_{0ij} F_1 + \frac{V_{0i} + V_{0j}}{2} + \frac{M_{0j} S_{0i} + M_{0i} S_{0j}}{8\pi} \quad (10)$$

where the $F$ functions now depend on $U_{0ij}/kT$ but are the same functions as those tabulated by Kihara for pure components.

In order to calculate $B_{ij}$ all the core parameters, $U_0/k$ and $\rho_0$ should be available for both pure components $i$ and $j$. These last two are then combined in the customary semiempirical fashion:

$$\rho_{0ij} = \frac{\rho_{0i} + \rho_{0j}}{2} \quad (11)$$

$$U_{0ij} = \sqrt{U_{0i}\, U_{0j}} \quad (12)$$

It is not necessary to devise mixing rules for the core parameters. The parameters $M_0$, $S_0$, and $V_0$ are combined in an exact mathematical fashion as shown in Equation (10).

## APPLICATIONS

The Kihara model may be used to correlate experimental volumetric data for a series of substances. For example Connolly has shown that the volumetric properties of the normal paraffins can be correctly given by the Kihara potential using the rectangular core model shown in Figure 8. More important however is the fact that the Kihara model may be used successfully to predict the volumetric properties of gaseous mixtures from properties of the pure components alone. Connolly has shown that the Kihara potential gives good predictions of the volumetric behavior of the hydrogen-benzene system over a considerable temperature range (*3*).

One of the most interesting applications of the Kihara potential however is in the prediction of $K$ values for heavy components at moderate or low temperatures and at advanced pressures. Equations (1), (2), and (3) show the relationship between $K$ values and virial coefficients, and hence an accurate knowledge of virial coefficients is sufficient to produce good predictions for $K$ values in those cases where the assumption of a liquid phase activity coefficient of unity is valid. This assumption is excellent whenever the component in question is present in excess in the liquid phase.

In order to illustrate this application of the Kihara potential $K$ values have been computed for several heavy components in a number of representative systems. The results of these computations are shown in Table 2 which also compares calculated with observed $K$ values.

The good agreement between calculated and experimental results shown in Table 2 indicates that the Kihara potential is a reliable tool for estimating certain quantities of interest in phase equilibria. Whenever the dominant nonideality is in the gas phase rather than in the liquid phase, the most important parameter is the virial coefficient $B_{ij}$ where $i$ and $j$ refer to different components. The parameter $B_{ij}$ reflects the intermolecular forces operating between the two different molecules, and hence it is the dominant quantity in determining the fugacity of a component present in small mole fraction in a compressed gas-phase mixture. The Kihara model is useful in predicting $K$ values because it is the basis of what appears to be a reliable technique for computing the important virial coefficient $B_{ij}$.

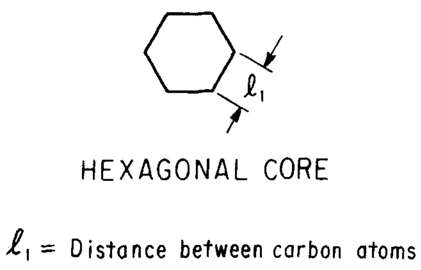

Fig. 7. Kihara core model for benzene.

While calculations for virial coefficients based on the Kihara model are probably the most reliable currently available, it seems that in highly asymmetric systems one of the core models given in Figure 8 is not adequate for mixture work. When equilibrium calculations for decane in hydrogen, nitrogen, and carbon dioxide are made with the core model proposed by Connolly, the calculated $B_{ij}$ $(i \neq j)$ values are always lower than those observed (*19*) by about 100 cc./g.mole. Connolly also found (*3*) that his computed $B_{ij}$ $(i \neq j)$ values for hydrogen-*n*-octane mixture were consistently below the experimental ones. It appears therefore that the core model of Connolly is very good for pure paraffins up to $C_8$ and for mixtures up to about $C_6$, but it is not suitable for mixture calculations with paraffins of high carbon number. It is likely that internal degrees of freedom, not accounted for in the core model, invalidate use of the Connolly core for large hydrocarbons; the larger molecule may bend or turn back on itself and

TABLE 2. *K* VALUES FOR HEAVY COMPONENT

| Components | | Temp., °C. | Total pressure, (lb./sq. in. abs.) | *K* (Heavy) | | Reference |
|---|---|---|---|---|---|---|
| Heavy | Light | | | Calculated | Observed | |
| *n*-pentane | methane | 38 | 200 | 0.115 | 0.113 | (*24*) |
| | | 71 | 400 | 0.163 | 0.169 | (*24*) |
| benzene | nitrogen | 75 | 905 | 0.027 | 0.026 | (*12*) |
| | | 100 | 911 | 0.053 | 0.049 | (*12*) |
| benzene | hydrogen | 50 | 442 | 0.0141 | 0.0139 | (*3*) |
| | | 50 | 638 | 0.0093 | 0.0090 | (*3*) |
| iso-octane | carbon dioxide | 50 | 300 | 0.0189 | 0.0171 | (*18*) |
| | | 75 | 300 | 0.0393 | 0.0396 | (*18*) |
| iso-octane | nitrogen | 50 | 1095 | 0.0085 | 0.0072 | (*18*) |
| | | 75 | 815 | 0.0188 | 0.0170 | (*18*) |
| iso-octane | hydrogen | 50 | 915 | 0.0047 | 0.0043 | (*18*) |
| | | 75 | 970 | 0.0110 | 0.0095 | (*18*) |

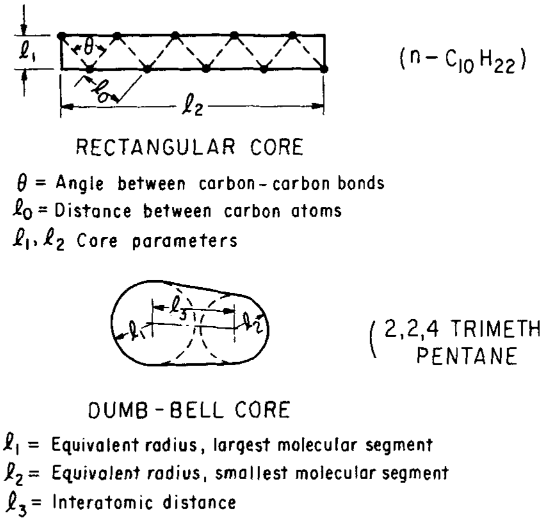

Fig. 8. Models of more complicated molecules.

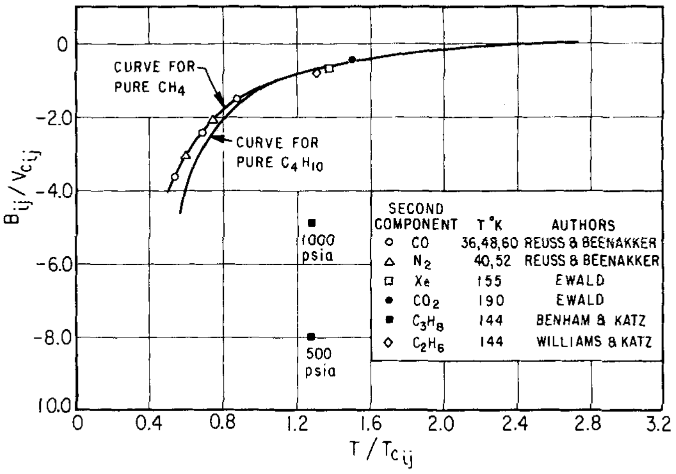

Fig. 9. Second virial cross coefficients for binary systems containing hydrogen.

clearly no allowance is made for this effect in the Kihara potential.

## THERMODYNAMIC CONSISTENCY

It has become increasingly common to test low-pressure phase-equilibrium data for thermodynamic consistency, but unfortunately this important practice has not as yet been widely adopted by experimentalists in the high-pressure field. A universal consistency test for high pressure data must be based on the Gibbs-Duhem equation, and recently Adler and co-workers (*1*) have reported a technique based on this equation where however they have unfortunately assumed validity of the incorrect Lewis fugacity rule. The virial equation of course is independent of the Gibbs-Duhem equation, but in certain cases where it is applicable it can provide the basis for a useful consistency test for a limited range of phase equilibrium data.

Consider a case where a heavy component *i* is in equilibrium with a light component *j* which is only sparingly soluble in the heavy component. In that case $\gamma_i$ is very nearly equal to unity, and from the experimental value of $K_i$ it is easily possible to compute $\phi_i$. However $\phi_i$ must be given by Equation (3), where all the individual coefficients (all the *B*'s and all the *C*'s) are independent of pressure and composition. If $K_i$ data are taken at one temperature but at different pressures, it is then possible to check if the fugacity coefficient $\phi_i$ has a pressure dependence in agreement with that dictated by Equation (3); if it does not, then the data cannot be consistent. Another way of expressing this consistency test is to say that a consistent set of isothermal $K_i$ data must give one and only one set of virial coefficients which is independent of pressure and composition.

The fact that the cross virial coefficients in Equation (3) are directly related to isothermal $K_i$ data has been the basis of a useful experimental technique for obtaining information on interactions between dissimilar species; by measuring the solubility of a liquid in a compressed gas it is possible to compute cross virial coefficients with an accuracy much higher than that obtained by conventional vapor-phase compressibility measurements (*19, 23*).

To illustrate the thermodynamic consistency test outlined above consider the data for the propane-methane-hydrogen system reported by Benham and Katz (*2*). At −200°F. these authors report *K* values for propane as follows:

| $x_0$ | $x_1$ | $x_3$ | $y_0$ | $y_1$ | $y_3$ | Total pressure, (lb./sq. in. abs.) | $K_3$ |
|---|---|---|---|---|---|---|---|
| 0.00789 | 0.0859 | 0.9062 | 0.9573 | 0.0379 | 0.0048 | 500 | $5.29 \times 10^{-3}$ |
| 0.0179 | 0.1014 | 0.8807 | 0.99 | 0.0037 | 0.0063 | 1,000 | $7.15 \times 10^{-3}$ |

Since propane predominates in the liquid phase, $\gamma_3 = 1$ and the *K* value for propane is given in accordance with

$$K_3 = \frac{f_3{}^L}{\phi_3 P} \tag{13}$$

with

$$f_3{}^L = \phi_3{}^0 P_3{}^0 \exp \frac{v_3{}^L (P - P_3{}^0)}{RT} \tag{14}$$

and

$$\ln z\, \phi_3 = \frac{2}{v} [y_0 B_{03} + y_1 B_{13} + y_3 B_{33}] + \frac{3}{2v^2} [y_0{}^2 C_{003} + y_1{}^2 C_{113} + y_3{}^2 C_{333} + 2y_0 y_1 C_{013} + 2y_1 y_3 C_{133} + 2y_0 y_3 C_{033}] \tag{15}$$

In the expansion given in Equation (15) the term in $1/v^2$ is probably negligible compared with the term in $1/v$ under the conditions prevailing in this case. To check this, estimates of all the coefficients were made with corresponding states correlations for $B_{03}$, $B_{13}$, $C_{003}$, and $C_{013}$ and with approximate calculations based on the square-well model for $C_{113}$, $C_{033}$, $C_{133}$, and $C_{333}$ as described by Hirschfelder, Curtiss, and Bird (*9*). The second virial coefficient for propane, $B_{33}$, was calculated with the Kihara potential and found to be −3,270 cc./g.mole.* When these coefficients and the experimental vapor-phase compositions are substituted into Equation (15), it becomes clear that, as expected, the term in $1/v^2$ is negligible compared with that in $1/v$ at both 500 and 1,000 lb./sq.in.abs.

In Equation (15) by far the most important term on the right-hand side is $y_0 B_{03}$, which is to be expected since it is the coefficient $B_{03}$ which reflects the interaction between propane molecules and hydrogen molecules in the vapor phase, and in the case being considered $y_0$ is much larger than either $y_1$ or $y_3$. The coefficient $B_{13}$ is characteristic of the methane-propane interaction and is well known from data on methane-propane mixtures. The coefficient $B_{33}$ for pure propane need not be known with high accuracy since $y_3$ is so small; however with the help of the Kihara potential it too can be computed with good certainty as indicated above. Hence the experimental data of Benham and Katz can be used to compute the important coefficient $B_{03}$, and if the data are consistent, then the value obtained must be the same at both pressures. When one uses the experimental *K* values, $B_{03}$ is found to be

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* The extrapolated equation of Pitzer and Curl gives −3,250 cc./g.mole.

| Pressure, lb./sq. in. abs. | $-B_{03}$, cc./g.mole |
|---|---|
| 500 | 856 |
| 1,000 | 505 |

The large difference between the two coefficients strongly suggests the possibility that the data at this low temperature do not represent true equilibrium conditions. This conclusion is furthermore supported by a comparison of $B_{03}$ as computed from the data of Benham and Katz with that obtained by the appropriate corresponding states correlation. Figure 9 shows a plot of the reduced second virial coefficient for methane and for butane; as expected the two plots are almost the same except at low reduced temperature where the effect of acentric factor becomes noticeable. Whereas the lines were obtained from pure component data, the points correspond to second virial cross coefficients taken from phase-equilibrium studies of various authors who investigated binary systems containing hydrogen. The reducing parameters $V_{c_{ij}}$ and $T_{c_{ij}}$ (for $i \neq j$) were computed in accordance with customary mixing rules.

Figure 9 shows clearly that the virial coefficients as determined from the data of Benham and Katz are much too low. In other words the experimental $K$ values are too large, by about two orders of magnitude. This result is, perhaps, not too surprising in view of the well-known difficulty of experimentally obtaining equilibrium $K$ values for heavy components at very low temperatures.

This analysis of experimental results is of particular interest because Motard and Organick (*14*) recently concluded that their correlation based on the Benedict-Webb-Rubin equation of state was invalid since it did not predict $K$ values for propane at low temperature in agreement with experiment. Figure 9 would suggest that this conclusion was erroneous and that in view of the experimental difficulties involved the experimental data are much more likely to be in error than the calculated results. If the virial equation is used and if all the coefficients are computed from the existing corresponding states correlations (plus the Kihara model for $B_{33}$), the following results are obtained:

| Pressure, lb./sq. in. abs. | $K$ for propane at −200°F. Benham and Katz | Motard and Organic | Corresp. states |
|---|---|---|---|
| 500 | $5.3 \times 10^{-3}$ | $9 \times 10^{-5}$ | $8.02 \times 10^{-5}$ |
| 1,000 | $7.16 \times 10^{-3}$ | $8 \times 10^{-5}$ | $7.87 \times 10^{-5}$ |

The two methods of computation are in very good agreement. The discussion above suggests that when one considers disagreement between experimental and calculated results in phase equilibria it is not always valid to assume that preference must be given to the experimental data.

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## NOTATION

$B$ = second virial coefficient
$C$ = third virial coefficient
$F$ = a function of $U_0/kT$
$f$ = fugacity
$k$ = Boltzmann constant
$K$ = $y/x$
$l$ = length parameter in Kihara core
$M_0$ = parameter characteristic of Kihara core
$N$ = Avogadro's number
$P$ = pressure
$P^0$ = vapor pressure
$R$ = gas constant
$R_1$ and $R_2$ = principal radii of curvature
$r$ = distance between molecular centers
$S_0$ = surface parameter characteristic of Kihara core
$v$ = molar volume
$V_0$ = volume parameter characteristic of Kihara core
$V^*$ = reduced volume
$V_c$ = critical volume
$T$ = absolute temperature
$T_c$ = critical temperature
$U$ = potential energy
$U_0/k$ = characteristic energy expressed as a temperature
$x$ = mole fraction in liquid phase
$y$ = mole fraction in vapor phase
$z$ = compressibility factor

### Greek Letters

$\rho$ = shortest distance between molecular cores
$\rho_0$ = shortest distance between molecular cores at energy minimum
$\rho^*$ = reduced density
$\gamma$ = activity coefficient in liquid phase
$\phi$ = fugacity coefficient in vapor phase
$\phi^0$ = fugacity coefficient ($f/P$ ratio) of pure component at its vapor pressure

### Subscripts

$i, j$ = to components
In last section:
0 = hydrogen
1 = methane
3 = propane

### Superscripts

$L$ = liquid phase

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