Equilibrium, Thermodynamic, and Transport Properties of Polyatomic Gases from Molecular Structure

The possibility of predicting physical properties for polyatomic gases entirely from molecular structure has been explored. Intramolecular force constants for the bonds can be drawn from spectroscopically established tables and applied successfully to molecules involving a large variety of structures. A vibrational analysis of the molecule using these constants yields the thermodynamic functions of the ideal gas. The intermolecular pair potential parameters for the spherical core model of Kihara can be obtained quantitatively from molecular constants, and this potential can be used in obtaining the dilute gas transport properties. A linear relationship was found between the Kihara spherical core size and Pitzer's acentric factor. Also from the Kihara model the critical constants are derived, which allows one to use Pitzer's compressibility tables for the dense gas corrections to the ideal gas law and the excess functions of the thermodynamic quantities. A complete package of computer programs which predict all important physical properties directly from input name alone has been written and tested. Suggestions are given for future work needed to improve many of the techniques presented.

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SCOPE

The present scheme was developed to determine just how far our current knowledge could take us toward achieving this goal of a priori properties prediction from molecular structure. We sought to strike a balance between computer information retrieval from a large data base and properties prediction. Automated computer methods for properties are an important part of all process design engineering computer systems used in industry, and there is a great economic incentive to reduce the associated storage and computation costs for properties. For the past decade nearly all proprietary systems were based on the AIChE Physical Properties Estimation System (APPES) developed for IBM 7094 equipment which has proved to be a very expensive operation.

Molecular structure information for a variety of molecules has become available in just enough detail to encourage development of new predictive methods for the physical properties. The kind of structural information needed is minimal, such as an accurate scale molecular model. This concept is directed toward future computer applications, when a user can enter the structural information at a remote console in a familiar language and select the type of properties desired and conditions of temperature, pressure, composition, etc. Even with no experimental data available to the user, predictions of physical properties may be possible.

CONCLUSIONS AND SIGNIFICANCE

The thermophysical properties for many species important in chemical engineering now can be computed with engineering accuracy given a cipher with only molecular structure information. The properties of rigid, spherically symmetric molecules are quite adequate, whereas those for aspheric, flexible species involving complex energy considerations require further work. Molecular volume computations through the Van der Waals atomic radii, the radii of gyration and the core size are surprisingly successful, as are the fundamental frequencies of vibration from structure. The computation of the energy of attraction through Slater-Kirkwood methods or simplified molecular orbital calculations is surprisingly dependent on molecular orientation for polyatomics. Further work is required in this area.

The use of the Kihara intermolecular potential and Pitzer's three-parameter law of corresponding states is adequate for the smaller, nonpolar hydrocarbons. For other species, force field parameters in addition to finiticity should include molecular asphericity, flexibility, polarity, dipole induction, dipole shielding, association, weak hydrogen bonding, etc. The three-parameter Joffe equation is useful for enthalpy, entropy, and heat capacity accounting for molecular finiticity, otherwise the straight

Redlich-Kwong equation is adequate. New equations of state are needed to account for the other force fields discussed above. This field is in its infancy, and offers promise in the future.

INTERMOLECULAR FORCE FIELD

The intermolecular potential model of Kihara, although far from accurate, provides a sound theoretical basis for the work of Pitzer (1955).

$$\psi(r) = 4\epsilon \left[\left(\frac{\sigma - 2a}{r - 2a} \right)^{12} - \left(\frac{\sigma - 2a}{r - 2a} \right)^{6} \right] \qquad (1)$$

Although the work of Pitzer in developing his famous compressibility tables was empirically based, more abundant data have become available today which strongly indicate a simple linear relationship between the Pitzer acentric factor and the Kihara spherical core parameter for nonassociated systems (Tee et al., 1966; Galloway and Sage, 1967). The concept of this Kihara model is based on molecular structure. The core of many polyatomic species can be approximated to be spherically symmetric. Kihara (1953) discussed various geometric models for the polyatomic core of a number of molecules and compared predictions of the virial coefficients with experimental data. This model has also recently been applied to transport properties (O'Connell, 1965; Barker et al., 1964; Galloway and Sage, 1967). Such determinations of the Kihara models for polyatomic gases from experimental virial coefficients as well as viscosities have yielded potential parameters which differ rather considerably from those of the Lennard-Jones form.

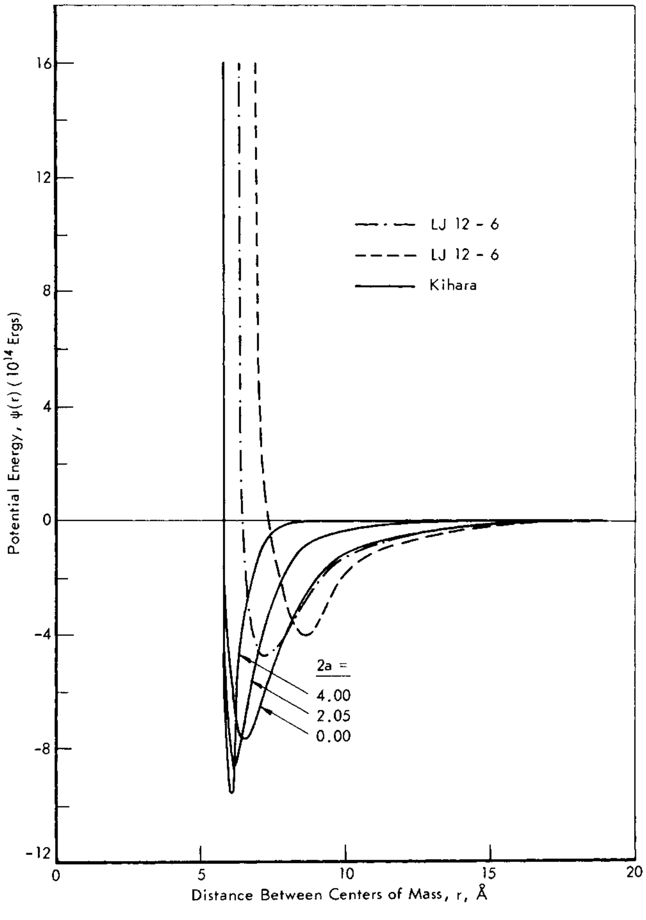

Fig. 1. Intermolecular potential for neopentane.

A polyatomic gas, which is spherically symmetric and ideally suited to the Kihara model, such as neopentane, has been examined in detail (O'Connell, 1965; Svehla, 1962). Figure 1 indicates the three potential functions determined for neopentane. The dotted curve was established for the Kihara model with a vanishingly small core, which corresponds to the Lennard-Jones 12-6 form, and is based upon viscosity coefficients (Svehla, 1962). The dashed curve, also for Lennard-Jones 12-6, was obtained from new virial work (O'Connell, 1965). These new virial data were also used to obtain the Kihara potential with a core size of 2.05A. Note how these three curves differ. The shape and position of the well depends very strongly upon the range of temperature covered in the experimental data used to determine the potential. For example, low temperature phenomena depend more strongly upon the attractive portions of the potential function while high temperature or high pressure phenomena depend upon the repulsive portion. Obtaining potential parameters from fitting experimental data suffers severely from the difficulty that there can be a large number of consistent pairs σ, ϵ/k which will reproduce data; however, the single value of one parameter alone will have a large confidence limit and may not correspond well with systematic variations in structure in an homologous series. This is another reason why there can be differences between the potential functions determined from virial coefficients and from transport properties. Also shown in Figure 1 are the Kihara potentials for varying core sizes. The steepening of the well can be seen as well as the shortening of the range of the attractive forces. The effect of the core size will be related to Pitzer's acentric factor later.

Other kinds of spherically symmetric force fields in addition to Kihara, accounting for molecular finiticity, can be contrived to account for molecular asphericity, flexibility, polarity (Mason and Monchick, 1962), dipole induction, dipole shielding, association, weak hydrogen bonding, etc. The Kihara model leads to a three-parameter law of corresponding states like Pitzer's (Lewis et al., 1961; Pitzer, 1955, 1956) without inclusion of molecules involving polar or association effects. The later effects have been removed from Pitzer's work (Thompson, 1966) leading to a new four-parameter law of corresponding states. Later an identical contribution was made (Halm and Stiel, 1967).

Following the suggestion (Thompson, 1966) that Pitzer's acentric factor is simply related to the radius of gyration for unassociated polyatomics, Figure 2 was prepared for illustrative purposes only. It shows the superficial relationship between the Kihara parameters and the radius of gyration. The sources of data are (O'Connell, 1965; Sherwood and Prausnitz, 1964; Galloway and Sage, 1967). Note that the core size is more nearly proportional to the radius of gyration than the collision diameter and also that the collision diameter resembles the core, only shifted to a higher value. Such behavior suggests that for these hydrocarbons, upon which most of the curve is based, this displacement may be related to the presence of the hydrogen atoms outside the carbon cage which may appear rather soft for such complicated structures.

A more fundamental approach for predicting the Kihara core from molecular structure is the geometrical technique (Kihara, 1953; de Rocco et al., 1967). They used a variety of geometric core models to compute the core size, $2a$. Some examples for which the Kihara parameters have been determined experimentally have been shown in Figure 3. For the larger more rigid structures, such as neopentane, the core is quite accurately given by the volume enclosed within the carbon cage. This core is determined from a distance from the center of mass to the carbon plus a distance to the hydrogen which is weighted by the square of the polarizabilities associated with carbon ($\alpha_C = 0.93 \times 10^{-24}$ cc.) and hydrogen ($\alpha_H = 0.42 \times 10^{-24}$ cc.). Such a weighting procedure is based upon the Slater-Kirkwood equation for dispersion forces (Hirschfelder et al., 1964).

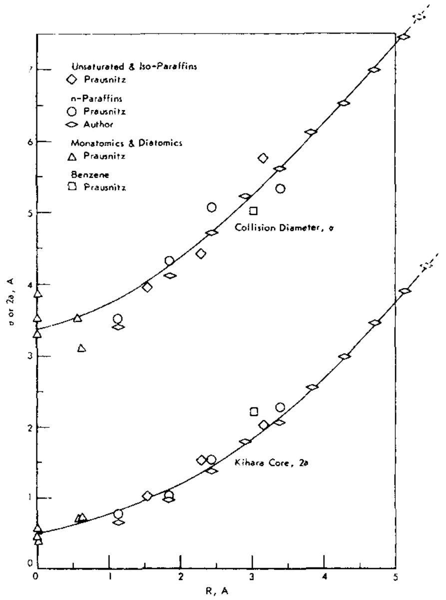

Fig. 2. Radius of gyration and intermolecular repulsion.

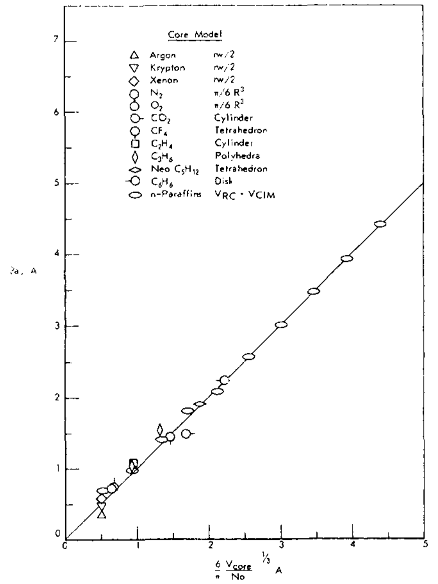

Fig. 3. Prediction of Kihara core from geometric models.

For the very flexible molecules, such as the normal paraffins, such a procedure will seriously underestimate the Kihara core. The paraffins are known to involve hindered rotation of the methyl groups as well as a rotation and bending about the carbon bonds. Such motion tends to sweep out a volume in addition to that occupied by the stationary structure. That is, the volume of the Kihara core is composed of two terms:

$$V_{KC} = \frac{\pi}{6}(2a)^3 = V_{RC} + V_{CIM} \tag{2}$$

The rigid core volume V_{RC} must correspond to the volume occupied by two bonded methyl groups (ethane), which possess a slight rotation effect but no volume from the internal motions V_{CIM} of the flexible chain. Propane is the first paraffin to exhibit such a carbon-carbon freedom of flexibility. The volume of the rigid core determined from the Kihara core of ethane was found to be

$$V_{RC} = 0.508\ A^3 \tag{3}$$

The core volume swept out from the internal motions is given by the following:

$$V_{CIM} = \frac{4}{3}\pi(r + nl)^3 \tag{4}$$

where the effective radius of the generator is given by two terms: the first r is that radius associated with the motion of the ends of the chain, and the second nl arises from the independent motion of n CH_2 groups acting at a radius l. From the available (Galloway and Sage, 1967) core sizes for the normal paraffins, the values of r and l were found to be constant within ±0.5% for the paraffins through n-decane.

$$r = 0.330\ A \tag{5}$$

$$l = 0.232\ A \tag{6}$$

The overall expression for the core size becomes

$$2a = \left\{ \frac{6}{\pi} \left[0.508 + \frac{4}{3}\pi(0.330 + 0.232n)^3 \right] \right\}^{1/3} \tag{7}$$

This relation was used in the predictions made in Figure 3 for the paraffins. Note that the values of r and l are well within the cross section of the methyl group; thus, the amplitude of this chain flexibility is not large. For other types of chain flexibilities similar relations are expected for homologous groups; however, considerably more fundamental work needs to be done in this area of internal motions.

A very successful correspondence can be seen in Figure 4 between the Kihara spherical core and the experimentally established acentric factor of Pitzer. It compares favorably with the work of Tee, Gotoh, and Stewart (1966). This plot is particularly useful when the acentric factor is available or can be obtained from vapor pressure data to obtain directly the Kihara core. Or, if the core can be computed from a geometric model, the acentric factor can be obtained. A comparison between Figures 2 and 4 show clearly that a relation between Pitzer's acentric factor and the radius of gyration is possible. Just such a correlation has recently been found (Thompson, 1966) to be very successful for a large variety of data. Undoubtedly this simple relation shown in Figure 4 is the basis behind Thompson's work for unassociated species. For highly polar and associated species the Kihara potential must have a Stockmayer term for dipole and quadrapole interactions added to the potential. Although limited virial coefficients have been obtained for such a potential (O'Connell, 1965) no collision integrals have been computed. Undoubtedly this polar parameter will correlate with Thompson's associated contribution to the acentric factor.

The last parameter for the intermolecular potential to be obtained from molecular structure is the well depth ϵ/K. The form of the intermolecular potential of Equation (1) arises from complete expressions (Hirschfelder et al., 1964) for the forces of repulsion and attraction which are expressed in the form of a series of alternating sign. Equation (1) is actually a first approximation to the series. Some of the positive terms from the attractive forces enter into the $1/r^{12}$ terms, and likewise some of negative terms of repulsion enter into the $1/r^6$ term. In this way, if one were to examine the coefficient of the $1/r^6$ term of the dispersion attractive forces, a good approximation to the well depth would be possible. There are a number of expressions for the dispersion forces which can be used; however, one of the most convenient is that of Slater and Kirkwood (Hirschfelder et al., 1964). The London dispersion energy is as follows:

$$E_L = \frac{-3e\hbar}{2m^{1/2}r^6} \frac{\alpha_A\alpha_B}{\left(\frac{\alpha_A}{N_A}\right)^{1/2} + \left(\frac{\alpha_B}{N_B}\right)^{1/2}} \tag{8}$$

where e is the electronic charge, $\hbar$ is Planck's constant divided by 2π, m is the electron rest mass, r is the interatomic distance, α is the electronic polarizability, and N the number of electrons in the outer shell.

Pitzer has used the Slater-Kirkwood expression to compute the coefficients for the inert gases (Pitzer, II, 1956). Pitzer (III, 1956) also correctly predicted the observed isomerization energies for the various configurations of the paraffins. Predictions (Prigogine, 1959) for the lighter elements differ slightly from the elements with more electron shells as shown on Figure 5. Duplicate points for the same species result from variations in the observed potential only. The Slater-Kirkwood expression only accounts for the outermost electron polarizability; however, for the more complicated elements the inner electrons can contribute substantially to the intermolecular potential attractive energy. The shielding effects of the outer electron shell, however, somewhat damp out the inner electron effects. Note that xenon differs from Slater-Kirkwood predictions considerably more than argon as a result of xenon's five electron shells compared to argon's three. Group V elements with five shells have well depths above Slater-Kirkwood predictions. For the hydrocarbons this problem is not so serious because of the small number of electron shells; however, for such polyatomics the orientation becomes important.

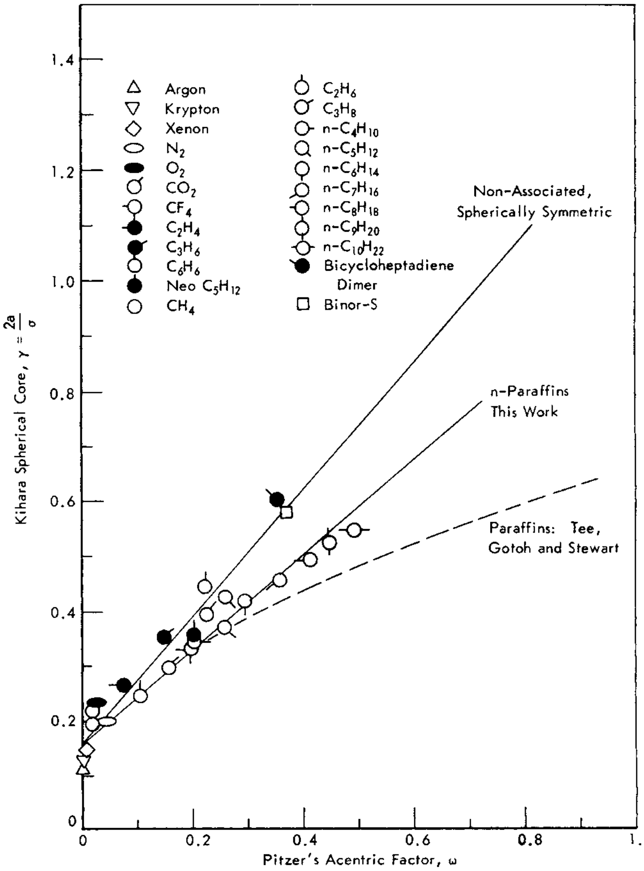

Fig. 4. The relation between the Kihara core and Pitzer's acentric factor.

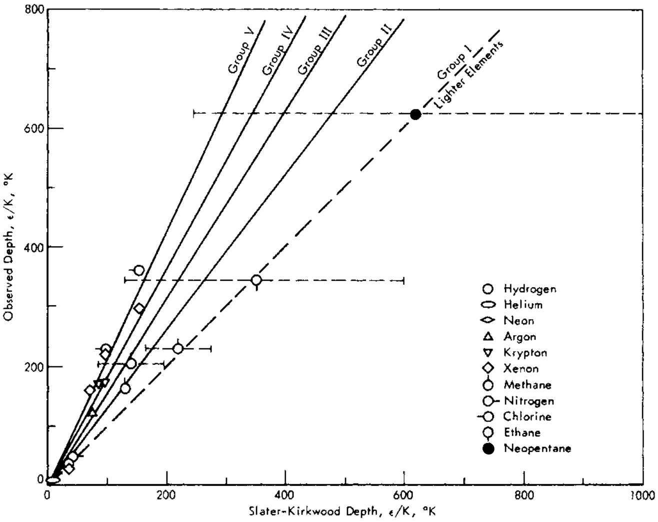

Fig. 5. Slater-Kirkwood energy of attraction.

Take the case of methane. Pitzer carried out the computations for methane as if it were a single attraction center. This is possible only because methane is nearly spherically symmetric and does not have a large number of electrons. The point without an attached uncertainty shown in Figure 5 is that obtained by Pitzer using the single attraction center approximation. The points shown for methane and ethane with their associated uncertainties were computed by the author using the complete Slater-Kirkwood expression summed between all possible atom pairs:

$$\frac{\epsilon}{K} = \frac{1}{4K}\left[22.6\Sigma R_{CC}^{-6} + 8.68\Sigma R_{CH}^{-6} + 3.42\Sigma R_{HH}^{-6}\right] \times 10^{-60}\ \text{ergs} \tag{9}$$

This computation was carried out by placing two polyatomics with a specific orientation at a distance between their center of mass corresponding to the observed potential minimum r_0. If r_0 is not available it can be obtained from the collision diameter and core size as described earlier. With the molecules in place, the interactions between the atomic electron clouds were summed up: carbon-carbon, carbon-hydrogen, and then hydrogen-hydrogen. The calculation depends strongly upon the relative orientations of the polyatomics. The range of values of well depth shown in Figure 5 for methane, ethane and neopentane arose from different relative orientations. Now for spherically symmetric molecules if all orientations in the collision process were equally probable then the well depth would be expected at the center of the range. The extreme values of ϵ/K for ethane are highly unlikely in the collision process, but the complete range is shown to clearly illustrate the importance of collision

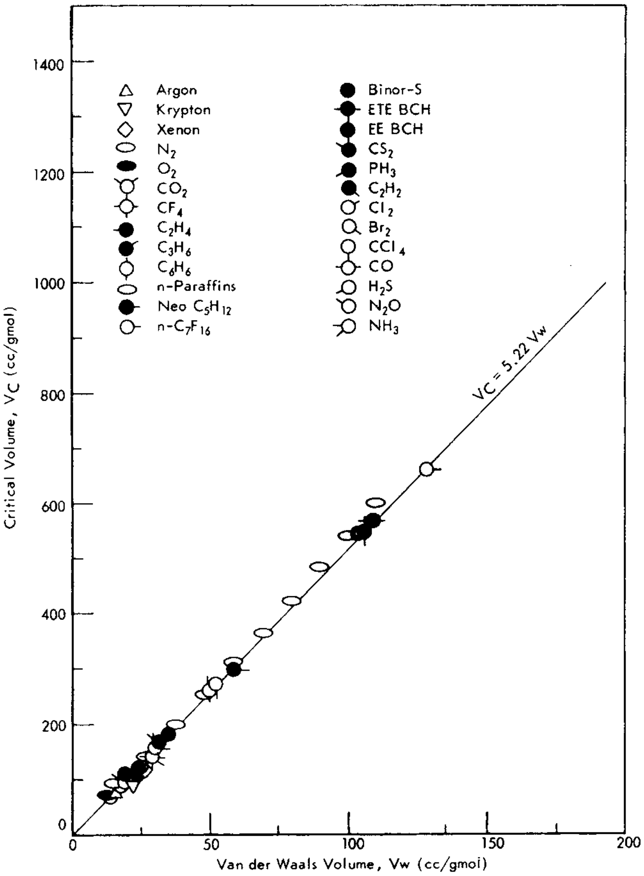

Fig. 6. The critical packing density.

orientation. Even neopentane which is highly spherically symmetric exhibits a large range of ϵ/K. This arises when the hydrogens and carbon are matched end on as opposed to when they are positioned between the three methyl groups. Orientation probabilities are now under study. Simplified molecular orbital calculations offer great promise for accounting for the inner shell electrons; however, orientation effects still remain as the big challenge.

Critical Constants

The molecular structure has long been known to be an important consideration in the critical constants for polyatomic gases, especially size effects (Stiel and Thodos, 1962). A more fundamental relationship involves the notion of a critical packing density which depends upon the electron distribution on the atomic level. In this way, the critical volume should be an invariant multiple of the Van der Waals volume (Bondi, 1964). Such a criteria has been examined in Figure 6 for a wide range of monatomics, diatomics, and polyatomics. There is a small tendency for the larger cage-like structures to possess a critical volume somewhat higher than expected from the Van der Waals volume obtained from atomic contributions, and this is expected from included volume considerations. On the whole, such a simple relationship works remarkably well

$$V_C = 5.22 V_w \tag{10}$$

For the Kihara potential, using the recent virial coefficient computations, a similar relation can be derived:

$$U_0/K = (0.292 + 0.510\gamma + 0.821\gamma^2) T_B \ ^\circ\mathrm{K} \tag{11}$$

where the reduced core size γ is just $2a/\sigma$. When one recalls Figure 4, the direct analogy of Equation (11) with Pitzer's concept becomes clear. The reduced Boyle point was found to be $T_B/T_C = 2.40$, almost identical to that found by others (Tee et al., 1966; Moelwyn-Hughes, 1957).

EQUILIBRIUM AND THERMODYNAMIC PROPERTIES

The previous discussion of intermolecular forces forms a basis for much of this discussion involving the virial equation and Pitzer's compressibility tables. Since we are dealing primarily with polyatomic molecules, the vibrations of the atoms within the structure governed by intramolecular forces also become important in predicting the equilibrium thermal properties, such as the heat capacity, enthalpy, and entropy.

Statistical Thermodynamics

The intramolecular vibrations in a polyatomic molecule are the basis for statistical thermodynamics: the prediction of the thermal properties from molecular structure. This science has been well worked out; only minor improvements need to be made. With the advent of our high speed, large core computers, and an accurate knowledge of the intramolecular force fields, a complete vibration analysis can be made on relatively complex structures. Detailed work has been done at Shell on the polyatomic force fields (Snyder and Schachtschneider, 1963, 1965; Schachtschneider and Snyder, 1963). For homologous series such as the normal paraffins an interatomic force constant for a rigid rotator, harmonic oscillator is very nearly invariant with wide variations in intramolecular environment; therefore, a small collection of constants serves well to describe many hydrocarbon structures. The results of these computations yields a complete set of fundamental and degenerate frequencies together with the symmetry number and principle moments of inertia. These can be used directly for computing the thermodynamic properties in the dilute gas state.

For complicated structures with a number of ringed portions, obtaining an accurate set of atomic Cartesian coordinates represents a problem. One solution that was used for the isomers of binor-s was to assemble accurate scale models of the structure and then photograph the structures with a long focal length telephoto lens in order to minimize the effects of parallax. These photographs were taken in normally two and occasionally three orthogonal planes. Transparencies were made to a scale so that one inch on the transparency corresponded to approximately one Angstrom in the model. The photographs were mounted in a Telereader, which is a device commonly used in mass spectra work where the individual *X-Y*, *X-Z*, or Y-Z coordinates could be measured. An IBM keypunch was programmed to punch directly the individual coordinates and keep track of the atomic species being measured. Identifying constants were also printed. A program written by Snyder (Snyder and Schachtschneider, 1963) was then used to convert these coordinates to a center of mass based system and then apply a scaling factor to insure that the interatomic distances (such as carbon-carbon) would be correct. This program computes the prolate ellipsoid volume formed through the hydrogen atoms and the volume of the carbon cage as well as the principle moments of inertia and radii of gyration. These coordinates are then used again for the normal coordinate vibrational analysis (Wilson et al., 1961).

Later a package of programs was developed (Bailey and Galloway, 1971) which made possible computation of Cartesian coordinates for the molecule directly from an input linear IUPAC cipher. This improvement was very successful and made possible the complete automation of the computation—from a name directly to the properties.*

The ideal gas thermodynamic properties are computed from the complete set of fundamental frequencies, the principle moments, and the symmetry number as follows: For a first approximation (Lewis et al., 1961) one can use the rigid-rotator-harmonic-oscillator model with no internal rotation or electronically excited states. Anharmonicity corrections can be made (Lewis et al., 1961) but are not usually important for temperatures below 2,000°K.

Such a thermodynamic computation using calculated frequencies was tested for a selected group of compounds for which thermodynamic properties were available (Rossini et al., 1953). A normal paraffin, a substituted paraffin, and a substituted cyclic were chosen, and a comparison was made in Figure 7. The heat capacity provides a severe test for these statistical mechanical computations as it becomes very sensitive to the values of the low frequencies, which are the most difficult to compute accurately. Effects of hindered internal rotation are apparent in Figure 7, as the accepted data for all three are greater than predictions around 350°K. The methyl substituted butane does indicate above 700°K increased effects of methyl rotation. These effects are also shown but to a lesser degree than n-butane. The substituted cyclohexane data are significantly higher at the higher temperatures, and apparently this arises from the puckering motion of the carbons around the ring. For these three polyatomics the entropy and enthalpy also compare favorably. These examples were selected as illustrative cases indicating the magnitude of the error to be expected for molecules with internal motion.

Pitzer's Compressibility Tables for Dense Gases

Pitzer (1956) has used the concept of the acentric factor, found to be so fundamental to the Kihara second virial coefficient, to generalize the virial equation as follows:

$$Z = \frac{PV}{RT} = Z^{(0)}(T_R, P_R) + \omega Z^{(1)}(T_R, P_R) + \ldots \qquad (12)$$

where $Z^{(0)}$ represents the well established behavior of a simple fluid, such as xenon or argon, and $Z^{(1)}$ the deviation function. Where the virial form fails miserably at elevated pressures owing to divergence, Equation (12) was found to be a substantial improvement when the reduced temperature functions $Z^{(0)}$ and $Z^{(1)}$ were taken to be functions of reduced pressure as well. Pitzer's tables of the compressibility factor (1956) PV/RT have been widely accepted and are considered to be the best available for unassociated species considering the number of input constants involved.

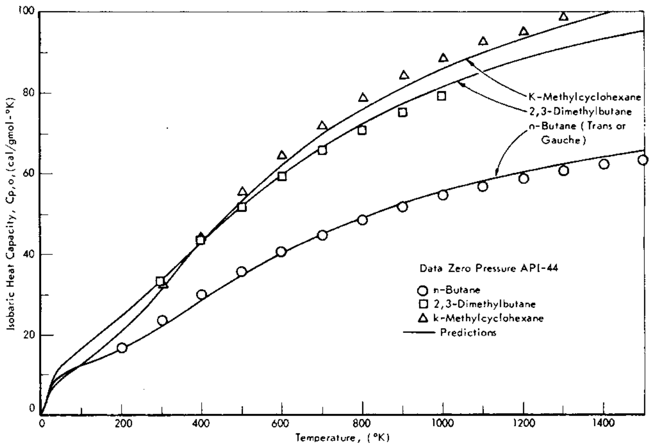

Fig. 7. Ideal gas heat capacity from molecular vibration analysis.

Now that we have a successful table of state properties based upon the molecular principles of the Kihara potential, all necessary parameters for these tables can indeed be obtained from molecular structure alone. To illustrate the improvement over an existing equation of state (Redlich-Kwong), take the critical compressibility factor. Redlich-Kwong predicts $Zc = 0.333$ regardless of the core size. For methane the observed value is 0.290 which is identical to Pitzer's prediction. For neopentane the observed is 0.269 and Pitzer's prediction is 0.275. Since the critical region is of such industrial interest such improvements may be important.

More recently the Joffe equation of state was modified (Barner and Adler, 1970) into a three-parameter form and it adequately reproduces Pitzer's tables for Z as well as fugacity, vapor pressure, and enthalpy. Only three parameters of T_c, P_c, and ω derived from molecular structure are required in order to compute the excess functions.

NONEQUILIBRIUM PROPERTIES

The shear viscosity, bulk viscosity, molecular diffusivity, thermal diffusivity, and thermal conductivity can be obtained for a wide range of polyatomic molecules in the dilute gas state using the intermolecular potential model of Kihara (O'Connell, 1965; Galloway and Sage, 1967). As molecular complexity increases, the Kihara model slightly underestimates the temperature dependence; however, this model is the best available and has been explored herein.

Viscosity of a Dilute Gas

For the polyatomics tested, n-decane proved to be the worst case with a standard error of 6.5% over a temperature range of 0° to 175°C. A long paraffin such as this is a complicated example, owing to chain flexibility. A standard error of about 4% was found for neopentane, so that not all of this deviation is expected from flexibility. Undoubtedly, the Kihara model fails to predict accurately the complete effects of the core in the collision process. The repulsion is probably all right but as was examined earlier in this paper, the attractive forces are longer range, and probably modeling with a core is an oversimplification of the complex force field in a polyatomic. For comparison, however, it should be noted that for polyatomics more complex than n-butane, a set of constants for the Lennard-Jones 12-6 potential simply cannot be obtained from experimental data using a technique described by Hirschfelder (1964) as the experimental temperature dependence is in excess of the square root and cannot be sufficiently counteracted by the entire collision integral. The presence of the core decreases the temperature dependence of the collision integral as shown earlier (Galloway and Sage, 1967), by a slight amount which is sufficient to fit the experimental data. Figure 8 illustrates well the increased differences between predictions as the polyatomic core size is increased (for example, acentric factor). Reid and Sherwood's predictions (1966) have been taken as representing the best engineering predictions available. Predictions for binor-S differ markedly mainly from uncertainties in the collision diameter. For dense caged struc-

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* Inquiries on program availability should be addressed to J. D. Heldman, Shell Development Company, Licensing Division, One Shell Plaza, Houston, Texas.

tures the collision diameter may be considerably smaller than would be expected from normal paraffins. Such a comparison clearly indicates the need for confirming experimental work.

Diffusivity of Dilute Gas

Currently, the coefficients of molecular diffusion available have not been of sufficient precision to accurately discriminate between the Lennard-Jones 12-6 and the Kihara potentials (Galloway and Sage, 1967).

Thermal Conductivity of a Dilute Gas

For large molecules, however, with a high degree of internal flexibility, the simple contributions of Eucken (1913) are not adequate (Galloway and Sage, 1967). A new relation is compared to experimental data in Figures 9 and 10. The theoretical basis of this relation and its applicability to hydrocarbons was shown by the author (Galloway and Sage, 1967) and others (Johnson and Huang, 1954; Lambert et al., 1955; Penn. State, 1964; Saxena et al., 1964; Trappenier, 1965). In this paper it is shown to be equally applicable to a wide range of other polyatomic gases. In Figure 9 is shown a comparison with Hirschfelder's and Eucken's predictions. Although it has been suggested (Stiel and Thodos, 1964) that these predictions represent the high and low temperature limits respectively, no systematic deviations in the data with temperature were detected.

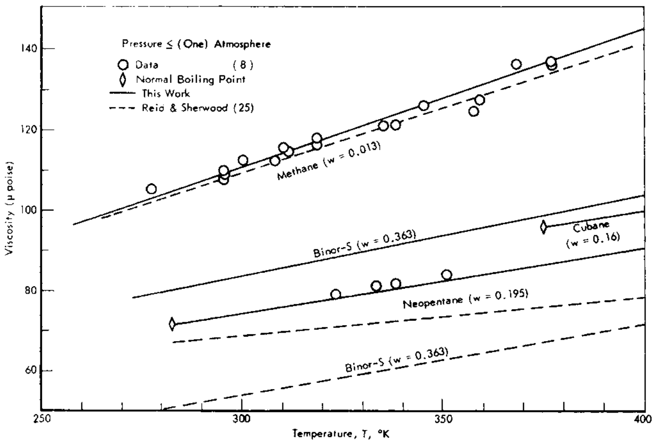


Fig. 8. Gas viscosity for selected caged molecules.

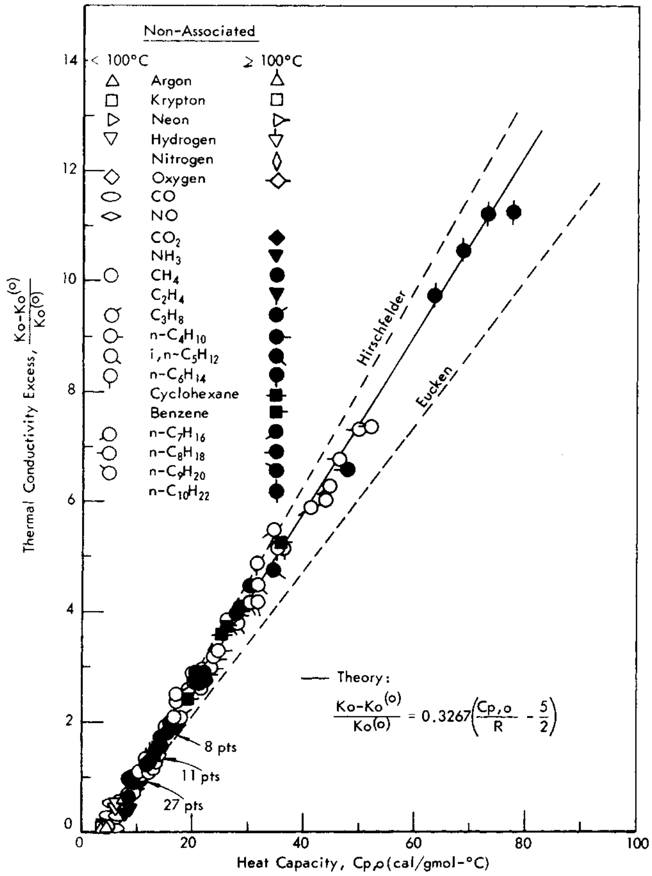


Fig. 9. The excess thermal conductivity.

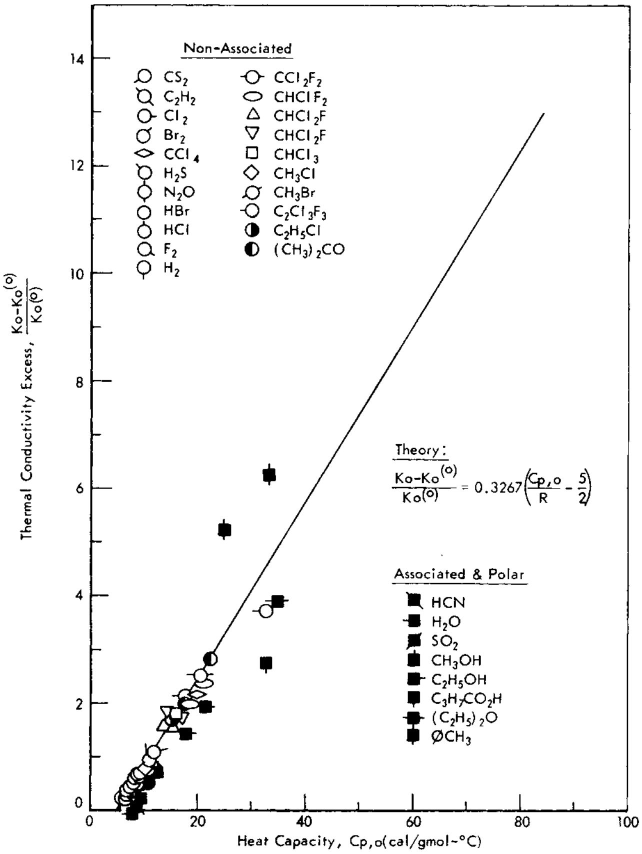


Fig. 10. The excess thermal conductivity for more complex polyatomics.

Figure 10 indicates the more uncertain data. The dark points denote polyatomic species which are known to be associated and polar. Other than toluene, these cases fall below predictions. It should be noted that for such complicated species the experimental heat capacity must be at such a sufficiently low pressure that none of the weak forces arising from association can contribute. Any such interaction would increase the heat capacity above the low pressure limit that must be used in this relation. It is believed that the toluene thermal conductivity may not be correct.

Dense Gas Corrections

Enskog (Hirschfelder et al., 1964) developed a kinetic theory for spherically symmetric, rigid molecules governed by an infinite repulsion and no attractive forces (Lennard-Jones ∞-0 potential if you prefer).

More recently Kirkwood (1935) and Born and Green

(1964) have proposed an alternate approach to that of Enskog. The viscosity is broken up into two terms: a kinetic term η_K which involves the transfer of momentum from the motion of molecules between collisions, and an intermolecular contribution η_ψ which involves momentum transfer as a result of the intermolecular force fields. The kinetic term must prevail at low pressures and, since this is a measure of the kinetic motion of the molecules, at dilution it must be a function of temperature alone. The potential term becomes more important at higher pressures. This theory is only in a redimentary state, however. Recently Rice and Gray (1965) have examined this potential term in the light of the square well potential, but no quantitative evaluations have been possible as yet. Because of mathematical difficulties, such an approach is not immediately useful, but it is certainly an important step.

Based on the arguments above, one might expect that the viscosity can indeed be broken up into two contributions; one which is independent of molecular size and arises from kinetic motion and one which might depend linearly on the molecular core size:

$$\eta_K = [\eta_0(T)] + [\nu^{(0)}(\rho^*) + \eta_\psi] \qquad (13)$$

$$\eta_\psi = \gamma\nu^{(1)}(\rho^*) \qquad (14)$$

where η_0 represents the limit of viscosity at high dilution, $\gamma^{(0)}(\rho^*)$ the effects of increased collisions from rigid sphere, point-mass molecular behavior, and $\gamma\nu^{(1)}(\rho^*)$ the effects of increased molecular core size on the collision mechanism. The coefficient γ is just the reduced core size, $2a/\sigma$ discussed earlier and ρ^* is a reduced density $\rho\sigma^3/m$.

If we assume a simple linear relationship between γ and ω as shown in Figure 4, and normalize by σ, m and ϵ, then Equations (13) and (14) can be written as

$$\frac{\eta - \eta_0}{\sigma^{-2}\sqrt{m\epsilon}} = f^{(0)}(\rho^*) - \omega f^{(1)}(\rho^*) \qquad (15)$$

Figure 11 shows the utility of such a relationship. The viscosity excess is reduced by increased molecular complexity. In Equation (15) the function $f^{(0)}(\rho^*)$ can be represented by the solid curve shown in Figure 11, and the function $f^{(1)}(\rho^*)$ can be represented by the theoretical based form (Reid and Sherwood, 1966; Rice and Gray, 1965):

$$f^{(1)}(\rho^*) = \rho^* - 0.100 \qquad (16)$$

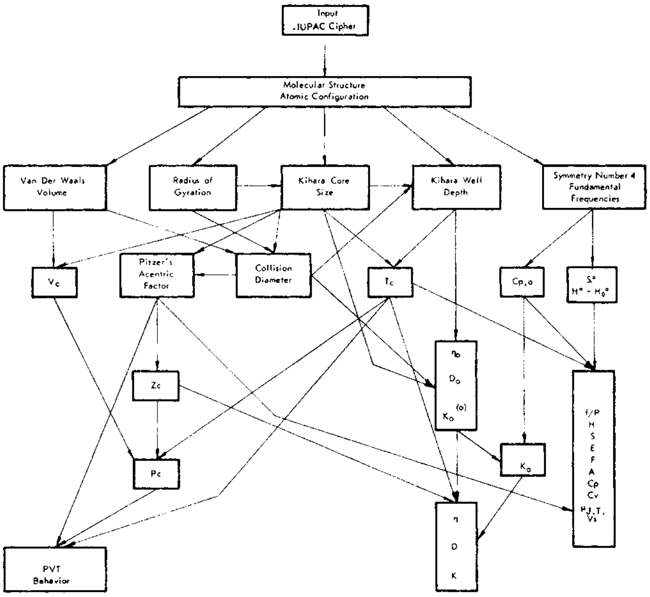
More experimental data are required for molecules that are relatively rigid and have a large core before this extended law of corresponding states can be developed further and be ultimately related to nonequilibrium statistical mechanics.

It is most interesting to note the close resemblance of the empirical results of Jossi, Stiel, and Thodos (Jossi, et al., 1962):

$$\frac{\eta - \eta_0}{Pc^{2/3}M^{1/2}/Tc^{1/8}} = f(\rho/\rho_c) \qquad (17)$$

From the theoretical arguments discussed above, it is clear that a method predicting the effects of pressure on the viscosity excess from molecular structure should be more accurate than a viscosity ratio method, since the ratio does not remain invariant with temperature. This viscosity excess approach also works satisfactorily for polar gases as well (Stiel and Thodos, 1964).

TABLE 1. SCHEME FOR GENERATION OF PROPERTIES FROM A NAME



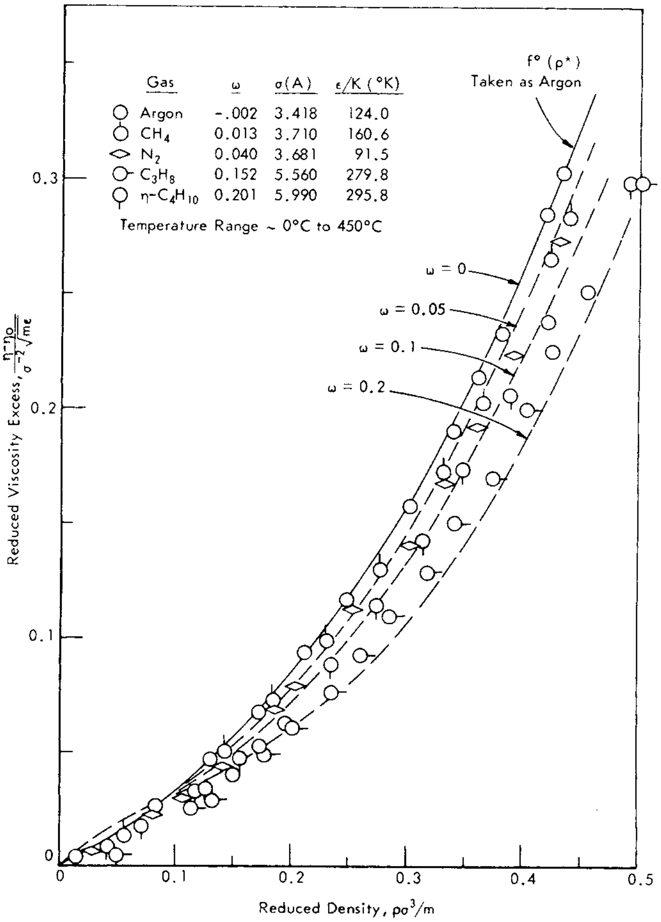


Fig. 11. Viscosity excess and core size.

Noting experimentally that the excess thermal conductivity is temperature invariant, the same approach has been found to be useful for high pressure conductivity as well (Stiel and Thodos, 1964). It is quite analogous to viscosity except that the excess depends much more strongly on the molecular complexity:

$$\frac{K - K_0}{Pc^{2/3}M^{1/2}/Tc^{1/8}} = \frac{1}{Zc^5}\, g(\rho/\rho_c) \qquad (18)$$

Enskog's theory applied to diffusion coefficients (Hirschfelder et al., 1964) has not been as conclusive as with viscosity, since the experimental data are very scattered and cover a temperature range less than 50°C.

A relationship of the ratio $D_{12}P/[D_{12}P]_0$ with the reduced density can be useful at moderate pressures, but it should only be used with caution at elevated pressures (above 80 atm.).

Mixtures

There are a number of mixing rules available for the transport properties (Reid and Sherwood, 1966) and they will not be discussed herein. However, it should be noted that all of these rules are strictly applicable for systems of species which are nearly spherically symmetric and not greatly dissimilar in nature. For greatly deviating species such rules fail badly (Galloway and Sage, 1967), but Chapman-Cowling kinetic theory has been shown to be much more successful (Galloway and Sage, 1967). For almost all these rules only quantities which we have discussed earlier, predictable from molecular structure, are required.

SUMMARY OF METHODS OF PREDICTION

The use of atomic configuration in the molecular structure has been summarized as follows for property predictions. The evolution of a physical property from input cipher (Bailey and Galloway, 1971) has been sketched in Table 1.

1. The sum of the Van der Waals Volumes for the atoms composing the polyatomic molecule can be obtained from known bond distances by a method such as that presented by Bondi (1964).
2. The collision diameter for the spherical core model of Kihara for the intermolecular pair potential may be computed from the radius of gyration correction (Figure 2).
3. The Kihara core for large, rigid polyatomic hydrocarbons is given quite adequately by the volume of the carbon cage for that molecule (Figure 3). For smaller molecules a small correction to the radius associated with the cage volume involving the square of the atomic polarizability increases this radius to a value lying between a radial hydrogen and the carbon atom. For flexible polyatomics corrections are presented for the volume swept out by these internal motions [Equation (7)]. The core can alternately be obtained from the radius of gyration (Figure 2) or the Kihara model core volume (Figure 3).
4. Pitzer's acentric factor can be obtained from a simple relationship to the Kihara core (Figure 4) or it can be estimated from the radius of gyration correlation of Thompson (1966).
5. The Kihara well depth can be estimated from a Slater-Kirkwood summation (Figure 5), although for species differing greatly from spherical symmetry other methods (Reid and Sherwood, 1966) may be more reliable.
6. The critical volume is obtained from the Van der Waals Volume (Figure 6).
7. The critical temperature can be estimated from the relation to the Kihara well depth and the Kihara core [Equation (11)].
8. The critical compressibility factor is computed from the acentric factor: $Z_c = 0.291 - 0.08\omega$ (Lewis et al., 1961).
9. The critical pressure can be computed directly from the three quantities above.
10. Fundamental frequencies of vibration are obtained from the Snyder and Schachtschneider (1963) computer program using the molecular structure.
11. The isobaric heat capacity and other thermodynamic functions for the ideal gas are computed from the fundamental frequencies of vibration within the polyatomic gas.
12. Nonideality corrections to the ideal gas thermodynamic functions are computed using Pitzer's techniques and analytic relations based on the Redlich-Kwong equation of state.
13. The dilute gas viscosity and molecular diffusivity are computed from the Kihara potential (Galloway and Sage, 1967; Hirschfelder et al., 1964).
14. The configurational thermal conductivity is computed from the Kihara model (Galloway and Sage, 1967).
15. Polyatomic corrections to the configurational conductivity can be applied from a knowledge of the heat capacity in order to compute the thermal conductivity of the dilute gas (Eucken, 1913; Galloway and Sage, 1967; Hirschfelder et al., 1964).
16. Dense gas corrections to the transport properties involving the excess properties are recommended (such as those of Thodos and co-workers conveniently presented by Reid and Sherwood (1966).
17. Mixtures can be treated using a knowledge of the pure component properties and other molecularly derived quantities presented above (Reid and Sherwood, 1966).

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NOTATION

a = radius of Kihara spherical core (Angstrom)
C_P = isobaric heat capacity, cal./g.-mole-°K
C_V = isochoric heat capacity, cal./g.-mole-°K
D = molecular diffusivity, cm^2/s
$f^{(1)}(\rho^*)$ = function of reduced density for excess viscosity
K = thermal conductivity, cal./cm-s-°K
k = Boltzmann's constant, 1.38045×10^{16} ergs/molecule-°K
M = molecular weight
m = molecular mass, g./molecule
N_0 = Avogadro's number (molecules/g.-mole)
n = number of CH$_2$ groups in a hydrocarbon
P = pressure, atmospheres
R = universal gas constant, 1.98726 cal/g.-mole-°K
$\bar{R}$ = radius of gyration from the geometric mean of the principle moments, Angstrom
R_{CC} = interatomic distance between a carbon atom in molecule A to that in B, Angstrom
R_{CH} = interatomic distance between a carbon atom in molecule A to hydrogen in B, Angstrom
R_{HH} = interatomic distance between a hydrogen in molecule A to hydrogen in B, Angstrom
r = intermolecular distance between the center of masses, Angstrom
$\bar{r}_w$ = Van der Waals radius obtained from the sum of the atomic Van der Waals volumes, Angstrom
T = absolute temperature, °K
T_B = Boyle temperature, °K
T_C = critical temperature, °K

U_0 = Kihara well depth, ergs/molecule
V = volume, cu.cm.
V_c = critical volume, cu.cm.
V_W = Van der Waals volume, cu.cm.
Z = compressibility factor
Z_c = critical compressibility factor
α = atomic polarizability, sq.cm.
γ = reduced Kihara core size, $2a/\sigma$
ϵ = intermolecular potential well depths, ergs/molecule
η = shear viscosity, micropoise
ν = a function of reduced density in Equations (13) and (14)
ψ = intermolecular pair potential function, ergs/molecule
ρ = density, g./cc.
σ = intermolecular potential collision diameter, Angstrom
ω = Pitzer's acentric factor

Subscript

A = atom A
B = atom B
C = value at the critical point
CIM = core generated from internal motions
KC = Kihara core
r = reduced quantity based upon critical point
RC = rigid core
0 = at condition of extreme dilution (for example, low pressure)

Superscripts

0 = ideal gas quantity
(0) = configurational quantity (no internal motion), or simple fluid
(1) = term denoting deviations from simple fluid

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