$[M]$ = monomer concentration, mole/liter

$[M\cdot]$ = total concentration of growing chains, mole/liter

$\overline{M}_n$ = number average molecular weight

$\overline{M}_w$ = weight average molecular weight

MW = molecular weight of monomer

r_{NM}, r_{PM} = polymerization rates for no mixing and perfect mixing, mole/liter · s

r_t, r_s, r_u, r_d = total polymerization rate, rate of sensitized photopolymerization, rate of unsensitized photopolymerization and rate of thermal polymerization, mole/liter · s

$[S]$ = photosensitizer concentration, mole/liter

x_l, x_h = fractions of low and high molecular weight species in polymer product

V_L, V_T = illuminated reactor volume and total reactor volume, liter

Greek Letters

ϵ_m, ϵ_s = molar absorptivities of monomer and sensitizer, liter/mole · cm

τ = optical thickness, V_T/V_L

ϕ = primary quantum yield, chains initiated/quantum absorbed

ϕ_{rate}, ϕ_{mw} = ϕ as determined by polymerization rate measurement and average product molecular weight measurement

ω = stirrer speed, rev./min.

LITERATURE CITED

Bamford, C. H., W. G. Barb, A. D. Jenkins, and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanisms,* Butterworth Science Publication, London, England (1958).

Bevington, J. C., *Radical Polymerization,* Academic Press, New York (1961).

Boundy, R. H., R. F. Boyer, S. M. Stosser, ed., *Styrene: Its Polymers, Copolymers, and Derivatives,* Reinhold, New York (1952).

Brandrup, J., and E. H. Immergut, ed., *Polymer Handbook,* 2 ed., pp. II-46-II-51, Wiley, New York (1975).

Chen, H. T., and F. B. Hill, "Radiation-Induced Polymerization in Continuous Stirred-Tank Reactors," *AIChE J.*, **17**, 933 (1971).

Felder, R. M., and F. B. Hill, "Mixing Effects in Chemical Reactors. I. Reactant Mixing in Batch and Flow Systems," *Chem. Eng. Sci.*, **24**, 385 (1969).

——————., "Mixing Effects in Chemical Reactors. II. Chain Reactions in Batch and Flow Systems," *Ind. Eng. Chem. Fundamentals*, **9**, 360 (1970).

Flory, P. J., *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York (1953).

George, M. H., "Styrene," *Vinyl. Poly.*, **1**, 139 (1967).

Hatchard, C. G., and C. A. Parker, "A New Sensitive Chemical Actinometer, II. Potassium Ferrioxalate as a Standard Chemical Actinometer," *Proc. Roy. Soc.*, **A235**, 518 (1958).

Hill, F. B., and R. M. Felder, "Effects of Mixing on Chain Reactions in Isothermal Photoreactors," *AIChE J.*, **11**, **873** (1965).

Hill, F. B., and N. Reiss, "Nonuniform Initiation of Photoreactions. II. Diffusion of Reactive Intermediates," *Can. J. Chem. Eng.*, **46**, 124 (1968).

——————., and L. H. Shendalman, "Nonuniform Initiation of Photoreactions, III. Reactant Diffusion in Single-Step Reactions," *AIChE J.*, **14**, 798 (1968).

Hutson, T., Jr., and R. S. Logan, "Development of a Photochlorination Reactor," *Chem. Eng. Progr.*, **68**, No. 5, 76 (1972).

Kawakami, W., and H. S. Isbin, "Effect of Agitation on Radiation Chemical Reaction Involving Chloral Hydrate Aqueous Solutions," *AIChE J.*, **16**, 502 (1970).

Kawakami, W., and S. Machi, "Effect of Mixing on Nonuniformly Initiated Polymerization by Radiation," *ibid.*, **19**, 94 (1973).

Klink, A., J. Lago, and E. Paul, "A Photochemical Reactor System," *Chem. Eng. Progr.*, **68**, No. 6, 81 (1972).

Mackay, M. H., and H. W. Melville, "Rate Coefficients in the Polymerization of Methyl Methacrylate (I)," *Trans. Faraday Soc.*, **45**, 323 (1949).

Mendiratta, S. K., "Mixing Effects in the Photosensitized Polymerization of Vinyl Monomers," Ph.D. thesis, North Carolina State University, Raleigh (1975).

———, and R. M. Felder, "Benzoin and Benzoin Methyl Ether-Sensitized Photopolymerization of Styrene and Methyl Methacrylate," Paper presented at the 67th Annual Meeting of the AIChE, Washington, D.C. (Dec. 1-5, 1974).

Muller, A. C., J. C. Eichacker, and F. B. Hill, "The Effects of Partial Illumination and Mixing on Sensitized Photopolymerization of Methyl Methacrylate," *BNL-16455* (1971).

Oster, G., and N. Yang, *Chem. Rev.*, **68**, 125 (1968).

Rushton, J. H., D. E. Mack, and H. J. Everett, "Displacement Capacities of Mixing Impellers," *Trans. Am. Inst. Chem. Engrs.*, **42**, 441 (1946).

Shah, M. A., and R. M. Felder, "Validity of Models for Annular Flow Photoreactors," *Paper No. 69C,* 64th Annual Meeting, AIChE, San Francisco, Calif. (1971).

Shendalman, L. H., and F. B. Hill, "Mixing Effects, Optimization and Dispersion Modeling in Bleachable and Sensitized Photoreaction Mixtures," *Chem. Eng. J.*, **2**, 261 (1971).

Yemin, L., and F. B. Hill, "Measurement of Mixing of Chain Centers in a Nonuniformly Initiated Photopolymerization," *Ind. Eng. Chem. Fundamentals,* **8**, 210 (1969).

Manuscript received April 2, 1975; revision received and accepted July 11, 1975.

Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules

SAMIL BERET and
J. M. PRAUSNITZ
Chemical Engineering Department
University of California,
Berkeley, California 94720

Generalized van der Waals theory is used to establish a partition function that considers the effect of density on rotational and vibrational motions in addition to translational degrees of freedom. A three-parameter equation of state is derived from this partition function. The equation of state is applicable to small, spherical (argon-like) molecules and also to

---

Samil Beret is now with Chemicals and Plastics, Union Carbide Corporation, S. Charleston, West Virginia 25303.

large, structurally complex molecules, including polymers. Parameters are presented for three polymers and twenty-two common fluids including light hydrocarbons, heavy hydrocarbons, nitrogen, carbon dioxide, hydrogen, carbon monoxide, hydrogen sulfide, sulfur dioxide, and water. The equation of state gives good liquid densities, and vapor pressures, and fair second virial coefficients.

SCOPE

Equations of state provide a useful tool for estimating thermodynamic properties of fluids. Empirical equations can give good results only if the numerous constants are determined from extensive experimental data. Theoretical equations require only limited experimental data, but the theoretical basis of such equations is limited either to small spherical molecules or, for more complex molecules, to a small density range.

A new equation of state, presented here, follows from a generalization of van der Waals theory, applicable to complex molecules at all fluid densities. The new equation of state is based on an interpolation between, on the one hand, perturbed-hard-sphere theory for small molecules (valid at all densities) and, on the other, Prigogine's theory for chain molecules (valid only at liquid like densities). The new equation of state contains three adjustable parameters reflecting molecular size (repulsive forces), molecular potential energy (attractive forces), and the number of external degrees of freedom, that is, those molecular motions which are affected by density.

Parameters are given for a variety of fluids. Results are presented for second virial coefficients, vapor pressures, saturated liquid volumes, and residual enthalpies.

CONCLUSIONS AND SIGNIFICANCE

The new equation of state holds for both gases and liquids; it is applicable to many fluids ranging in molecular complexity from hydrogen and methane to large hydrocarbons and polymers, including carbon dioxide, hydrogen sulfide, sulfur dioxide, and water. Like all analytical equations of state, the new equation is not good in the critical region.

Despite its theoretical basis, the new equation of state is in closed algebraic form without the cumbersome integrals that characterize most modern theories of fluids.

The equation of state presented here, using only three adjustable parameters, is useful primarily for estimating thermodynamic properties of fluids containing large molecules. For such fluids, experimental data are scarce, and, because of severe deviation from spherical shape, the molecules of these fluids exercise rotational and vibrational degrees of freedom which are density-dependent. The new equation of state, unlike others, takes these degrees of freedom into account.

Quantitative calculations in chemical process design require reliable estimates of thermodynamic properties. As discussed in numerous texts, an equation of state provides one possible tool for obtaining such properties for fluids. As a result, the literature is rich with articles describing a large variety of equations of state. In this work we propose one more such equation, but, as shown below, this new equation incorporates a few radically new features which may be particularly useful for some engineering purposes. Our new equation is applicable to fluids containing complex as well as simple molecules over a wide range of density including the compressed liquid. Our experience so far is primarily for nonpolar fluids, but we have also obtained good results for a few polar fluids, including water.

Equations of state for fluids can be broadly classified into two categories: empirical and theoretical, although some equations, with at least a modest claim to a theoretical basis, are sometimes called semiempirical. Empirical equations are useful primarily for presenting experimental data in analytical form, thereby facilitating integration and differentiation of the data to obtain desired thermodynamic properties. A well-known example of such an equation of state is the Benedict-Webb-Rubin (BWR) equation, which contains eight adjustable parameters. In recent years various extensions of the BWR equation have been presented, increasing both the mathematical complexity and the number of adjustable parameters. For example, the equation of Gosman (Gosman et al., 1969) requires sixteen constants to represent the properties of argon, while that of Bender (1973), also for argon, requires twenty constants.

While empirical equations of state are plentiful, theoretical equations are rare. Among these, best known is the virial equation of state, which, however, has only limited engineering utility since in practice it can be used only for low or moderate vapor densities; it is not applicable to dense gases or liquids.

Essentially all other theoretical equations of state are modern expressions of physical concepts first suggested by van der Waals over 100 years ago. These equations are often called *perturbed–hard-sphere* equations (Reed and Gubbins, 1973) because they are based on the fundamental assumption that the microstructure of a fluid is determined primarily by the repulsive forces of the molecules (that is, by the molecular diameters); once this microstructure is determined as a function of density, the effect of attractive forces can then be calculated by assuming that the molecules are situated in a uniform average field of force. In this context, *uniform* means that the field is both homogeneous and isotropic; the force at any one point and in any one direction is the same as that at any other point and in any other direction. The field strength for a given fluid depends on temperature and density.

In recent years much attention has been given by physicists to the details of calculating the effect of density on the structure of nonattracting (hard-sphere) molecules and the effect of temperature and density on the field strength. With very few exceptions, however, such calculations have been limited to small, spherically symmetric (argon-like) molecules. Carnahan and Starling (1972) have shown how two particularly simple forms of the perturbed–hard-sphere equation may be applied to practical engineering calculations for simple nonpolar fluids. In principle, but not always in practice, perturbed–hard-sphere equations apply to the entire range of fluid densities.

Little attention has been given toward development of a theoretical equation of state for fluids containing large

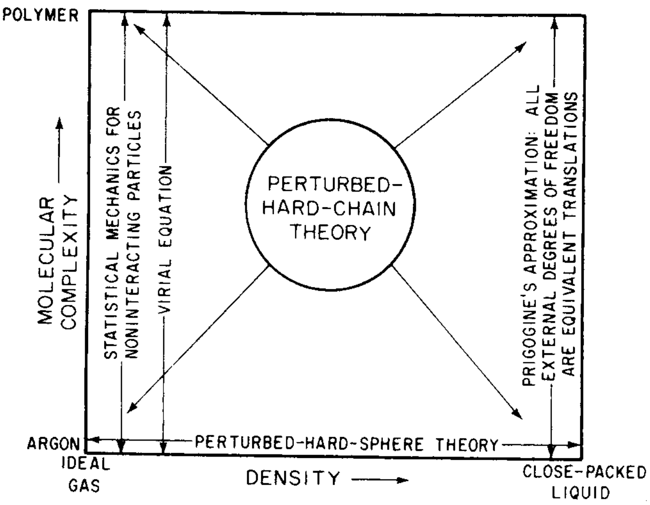


Fig. 1. Perturbed hard-chain theory provides an equation of state for fluids containing simple or complex molecules, covering all fluid densities.

TABLE 1. KEY EQUATIONS FROM PARTITION FUNCTION

SECOND VIRIAL COEFFICIENT*

$$\frac{B}{rv^*c} = 2.96 - \frac{7.03}{T} - \frac{3.52}{T^2} - \frac{1.17}{T^3} - \frac{0.29}{T^4}$$

Vapor Pressure

$$\tilde{P} = \left(\frac{\tilde{T}}{\tilde{v}^G - \tilde{v}^L} \right) \left\{ 1/c \ln \frac{\tilde{v}^G}{\tilde{v}^L} + \left[\frac{(\tau/\tilde{v})\ (3\tau/\tilde{v} - 4)}{(1 - \tau/\tilde{v})^2} \right]^G - \left[\frac{(\tau/\tilde{v})\ (3\tau/\tilde{v} - 4)}{(1 - \tau/\tilde{v})^2} \right]^L \middle| - \frac{W^G}{\tilde{T}} + \frac{W^L}{\tilde{T}} \right\}$$

Residual Enthalpy†

$$\frac{H^R}{R\left(\frac{\epsilon q}{k}\right)} = W - \tilde{T}\left(\frac{\partial W}{\partial \tilde{T}}\right)_{\tilde{v}} + \tilde{P}\tilde{v} - \frac{\tilde{T}}{C}$$

Residual Entropy**

$$\frac{S^R}{R} = -c\left(\frac{\partial W}{\partial \tilde{T}}\right)_{\tilde{v}} + c\frac{(\tau/\tilde{v})\ (3\tau/\tilde{v} - 4)}{(1 - \tau/\tilde{v})^2}$$

Fugacity

$$\ln\frac{f}{P} = \ln\frac{\tilde{T}}{c\tilde{P}\tilde{v}} + c\left\{ \frac{(8\tau/\tilde{v}) - 9(\tau/\tilde{v})^2 + 3(\tau/\tilde{v})^3}{(1 - \tau/\tilde{v})^3} \right\} + \frac{c}{\tilde{T}}\left[W - \tilde{v}\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} \right]$$

$$W \equiv \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{A_{nm}}{\tilde{v}^m}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right)$$

$$\left(\frac{\partial W}{\partial \tilde{T}}\right)_{\tilde{v}} \equiv -\frac{1}{\tilde{T}^2}\sum_{m=1}^{9}\frac{A_{2m}}{\tilde{v}^m} - \frac{2}{\tilde{T}^3}\sum_{m=1}^{5}\frac{A_{3m}}{\tilde{v}^m} - \frac{3}{\tilde{T}^4}\sum_{m=1}^{4}\frac{A_{4m}}{\tilde{v}^m}$$

$$\left(\frac{\partial W}{\partial \tilde{v}}\right)_{\tilde{T}} = -\sum_{n=1}^{4}\sum_{m=1}^{M}\left(\frac{mA_{nm}}{\tilde{v}^{m+1}}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right)$$

* See page 3029 of Alder (1972).

† $H^R \equiv H(T, V) - H^{\text{ideal}}(T)$.

** $S^R \equiv S(T, V) - S^{\text{ideal}}(T, V)$.

Superscripts G and L refer to gaseous and liquid phases.

polyatomic molecules because such molecules, in addition to translation, can also exercise rotational and vibrational motions which depend on density and, therefore, contribute to the equation of state. By contrast, argon-like molecules have only translational degrees of freedom since they neither rotate nor vibrate. Small molecules (for example, nitrogen, methane) have rotational and vibrational degrees of freedom, but since these, with little error, can be considered independent of density for normal fluid densities, perturbed–hard-sphere theory often provides a good approximation for fluids containing simple polyatomic molecules.

On the other hand, physical chemists interested in liquid polymers have developed theoretical equations of state suitable for very large molecules but restricted to liquid-like densities (Prigogine, 1957; Hijmans, 1961; Flory, 1970; Patterson and Delmas, 1970). All of these are based on an ingenious simplifying assumption proposed by Prigogine, namely, that at high densities, all density-dependent degrees of freedom can be treated as equivalent translational degrees of freedom. For example, the equation of state proposed by Flory (1970) combines Prigogine's treatment with that of van der Waals, but it is useful for both polymers and monomers only at high densities. It gives qualitatively incorrect results at low densities since, at zero density, it does not approach the ideal-gas law.

With respect to theoretical equations of state, the present situation may be described by the diagram shown in Figure 1.

At low densities, theoretical methods are available for calculating thermodynamic properties of a variety of molecules, including those possessing high molecular complexity (Hill, 1962; Reed and Gubbins, 1973).

For large molecules, where rotational and vibrational degrees of freedom depend significantly on density, Prigogine's assumption leads to a useful theoretical equation of state, which, however, is restricted to high (liquid-like) densities.

The purpose of this work is to establish a theoretically based equation which is valid for simple and complex molecules and for the entire array of fluid densities, ranging from the ideal gas to liquids and highly compressed gases. Upon suitably combining Prigogine's approximation with perturbed–hard-sphere theory, we have constructed a perturbed–hard-chain theory which yields the new equation of state. The advantage of such an equation of state is that it enables the design engineer to estimate thermodynamic properties of a large variety of fluids using only limited experimental data. One equation alone can be used for classes of fluids whose molecules range in complexity from, say, methane through eicosane or anthracene to polyethylene or polystyrene. One equation, applicable to both gases and liquids, and requiring only three adjustable molecular parameters, can provide good estimates of the thermodynamic properties of numerous fluids such as those shown in Table 1.

The statistical-mechanical derivation of the new equation of state is outlined in the next section. Readers concerned only with application may go directly to the section following Equation (13).

PARTITION FUNCTION

As discussed in any text on statistical mechanics, the equation of state is directly related to the partition function Q by

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} \tag{1}$$

The generalized van der Waals partition function (Vera and Prausnitz, 1972; Hill, 1962) is

$$Q = \frac{1}{N!} \left[\frac{V_f}{\Lambda^3} \right]^N [q_{r,v}]^N [\exp - \phi/2kT]^N \tag{2}$$

Contributions from translational degrees of freedom are given by the first bracketed term, where Λ is a constant depending on temperature.

For argon-like molecules, the quantity $q_{r,v}$ is independent of volume, and therefore, as indicated by Equation (1), it does not contribute to the equation of state. However, for polyatomic molecules, this frequently made simplifying assumption is not valid. The extent to which a molecule can rotate depends on whether or not that molecule is all alone or is surrounded by other molecules; in other words, the extent to which rotation can be exercised depends on density. The ability of atoms within a molecule to vibrate is also affected by the presence of near neighbors, although that effect is much smaller than the effect of near neighbors on rotations.

EXTERNAL DEGREES OF FREEDOM

Following Prigogine, we factor the contributions from rotational and vibrational degrees of freedom into an internal part and an external part:

$$q_{r,v} = q_{\text{int}} \cdot q_{\text{ext}} \tag{3}$$

where q_{int} depends only on temperature, but q_{ext} depends also on density. Again, following Prigogine, we want at liquid-like densities to consider external rotational and vibrational degrees of freedom as equivalent translational degrees of freedom; the total number of external degrees of freedom is designated by $3c$. For argon-like molecules, $c = 1$, and for all other molecules $c > 1$. Parameter c reflects the extent to which a molecule can exercise rotational and vibrational motions which are affected by the presence of neighbors. Indirectly, therefore, c is often a measure of molecular size because a large molecule has more external rotations and vibrations than a small molecule. However, more properly, parameter c reflects the looseness (or flexibility) of a molecule. Thus, parameter c for a stiff rod is smaller than that for a soft (rubber-like) rod having the same dimensions.

To find a suitable function for q_{ext}, we note first that there are four boundary conditions that must be satisfied:

In the ideal-gas limit, as $V \to \infty$, for all values of c

$$\frac{V_f}{\Lambda^3} q_{\text{ext}} \to \frac{V}{\Lambda^3} \tag{4}$$

In the close-packed liquid limit, as $V \to V_0$, for all values of c

$$\frac{V_f}{\Lambda^3} q_{\text{ext}} \to 0 \tag{5}$$

where V_0 is the closest-packed volume (largest possible density).

Equation (4) is necessary to obtain the ideal-gas law as the volume becomes very large. Equation (5) says that when the molecules are packed as densely as possible, all external degrees of freedom are locked in; that is, the molecule cannot exercise any motions.

For simple fluids, for all fluid densities, as $c \to 1$

$$q_{\text{ext}} = 1 \tag{6}$$

and the free volume V_f is given by an expression obtained from Carnahan and Starling (1972). (See also Vera and Prausnitz, 1972.)

$$V_f = V \exp \left[\frac{(\tau/\tilde{v})(3\tau/\tilde{v} - 4)}{(1 - \tau/\tilde{v})^2} \right] \tag{7}$$

Here τ is a numerical constant ($\tau = \pi\sqrt{2}/6 = 0.7405$), and $\tilde{v}$ is a reduced volume defined in Equation (10). The Carnahan-Starling equation holds for the fluid density $0 < \tilde{v}^{-1} < 0.6$, which corresponds to typical densities encountered in chemical engineering.

Finally, to obtain Prigogine's result for large molecules at liquid-like densities, it is necessary that

$$\frac{V_f}{\Lambda^3} q_{\text{ext}} \to \left(\frac{V_f}{\Lambda^3} \right)^c \tag{8}$$

Equation (8) says that at liquid-like densities all external and rotational degrees of freedom can be considered as equivalent translational degrees of freedom.

To meet these boundary conditions, we now postulate the simplest possible function for q_{ext}:

$$q_{\text{ext}} = \left(\frac{V_f}{V} \right)^{c-1} \tag{9}$$

where V_f is given by Equation (7). Equation (9) clearly satisfies the boundary conditions given by Equations (4), (5), and (6). Equation (9) also satisfies the boundary condition given by Equation (8) when we assume that liquids remote from critical conditions are essentially incompressible.

For large molecules it is convenient mentally to divide the molecule into r segments of equal size. The reduced volume is therefore defined by

$$\tilde{v} = \frac{V}{Nrv^*} \tag{10}$$

where v^* is the close-packed volume per segment. For hard-sphere molecules, $r = 1$, and v^* is related to the hard-sphere diameter d by

$$v^* = d^3/\sqrt{2} \tag{11}$$

The hard-core volume rv^* is closely related to the familiar van der Waals constant b.

POTENTIAL FIELD

The energy of interaction between a pair of molecules is a sensitive function of the intermolecular distance between them. To obtain an expression for the potential field ϕ, we must know how the molecules are positioned in space; this information is given by the radial distribution function. The original van der Waals theory assumes that the radial distribution function is independent of density and temperature. This assumption leads to the conclusion that intermolecular energy must be proportional to the density. However, x-ray scattering data have shown that while the radial distribution function depends weakly on temperature, it depends strongly on density. For the intermolecular potential field ϕ, we use the molecular-dynamic results of Alder (Alder et al., 1972) for molecules whose intermolecular forces are represented by the square-well potential, with a well width equal to one-half the diameter of the molecule. As shown by Alder, molecular dynamics avoids the problem of explicitly using radial distribution

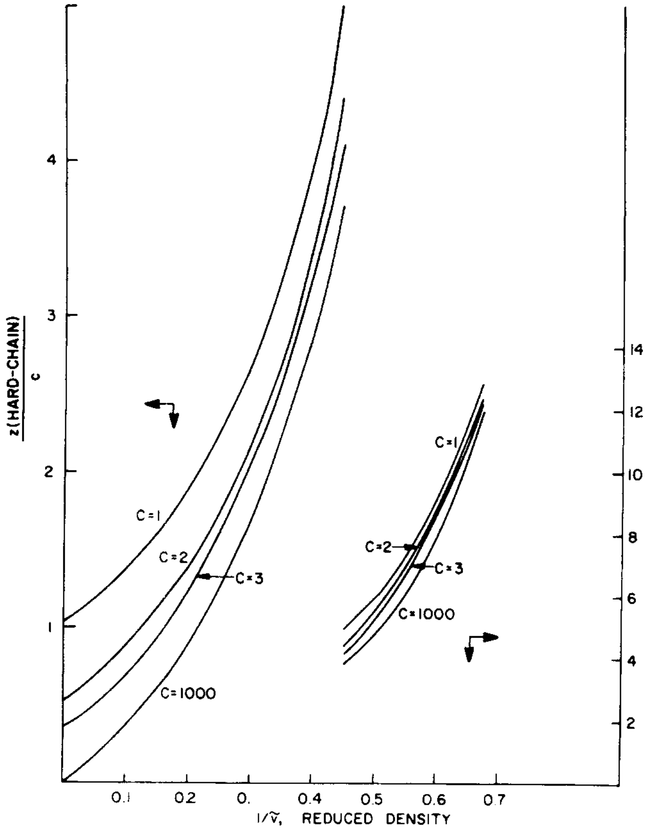


Fig. 2. Compressibility factor for hard-chain fluids depends on reduced density $1/\tilde{v}$ and number of external degrees of freedom 3c.

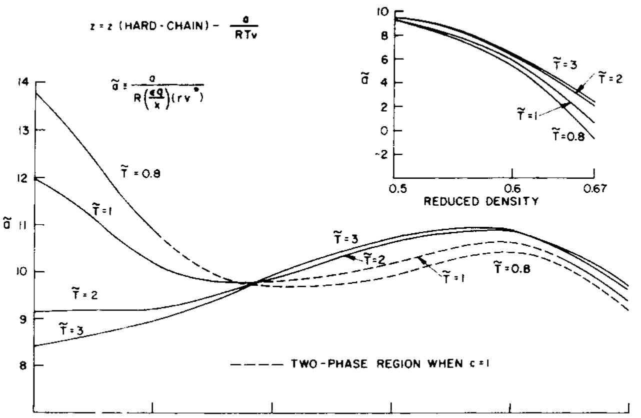


Fig. 3. Reduced van der Waals constant a depends on $\tilde{T}$ and $\tilde{v}$.

functions. Alder's results may be written in the form

$$\frac{\phi}{2} = \epsilon q \, W(\tilde{T}, \tilde{v}) \tag{12}$$

where ϵq equals characteristic energy per molecule, energy parameter ϵ is per external molecular segment, and parameter q is proportional to the external surface area of a molecule. (For pure fluids, the two parameters ϵ and q always appear together, as a product.) The analytical function W depends on reduced volume $\tilde{v}$ ($\tilde{v} \gtrsim 1.5$) defined by Equation (10) and on reduced temperature $\tilde{T}$, here defined by

$$\tilde{T} = \frac{T}{T^*} = \frac{ckT}{\epsilon q} \tag{13}$$

Equation (13) gives a measure of the ratio of kinetic energy to potential energy per molecule. Details for W are given in the Appendix.

EQUATION OF STATE

Substitution of Equations (2), (3), (7), (9), and (12) into Equation (1) gives the new equation of state. We write it in the familiar form of the van der Waals equation of state

$$z = z(\text{hard chain}) - \frac{a}{RTv} \tag{14}$$

where compressibility factor z is defined in the usual way:

$$z = \frac{Pv}{RT} \tag{15}$$

$$z(\text{hard chain}) = 1 + c\,\frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1 - \tau/\tilde{v})^3} \tag{16}$$

Van der Waals constant a is, in fact, not constant but depends on $\tilde{v}$ and $\tilde{T}$:

$$a = -R\left(\frac{\epsilon q}{k}\right)(rv^*) \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{mA_{nm}}{\tilde{v}^{m-1}}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right) \tag{17}$$

Coefficients A_{nm} are dimensionless constants given in the Appendix. These constants are independent of the nature of the molecules.

z(hard chain) takes into account the effect of repulsive forces on deviation from ideal-gas behavior. It depends strongly on reduced density $\tilde{v}^{-1}$ and on parameter c as shown in Figure 2.

The second term on the right-hand side of Equation (14), often called the *perturbation contribution*, takes into account the effect of attractive forces. Reduced van der Waals constant $\tilde{a}$ is shown in Figure 3. At low densities and high temperatures, $\tilde{a}$ is nearly constant as in the original van der Waals theory. As density rises, $\tilde{a}$ falls, approaching zero at very high densities corresponding to highly compressed liquids. For typical chemical engineering problems, the reduced density range is between zero and 0.55.

SOME PROPERTIES OF THE NEW EQUATION OF STATE

Equation (14) is the new equation of state. Unlike other theoretical equations for real molecules at high densities, it is algebraically simple and requires no integrations.

Equation (14) has only three adjustable parameters: rv^*, $(\epsilon q/k)$, and c. These parameters are obtained from data reduction as outlined below. For application to pure components, it is not necessary to split the two products rv^* and ϵq. However, such separation is necessary for application to mixtures as discussed in a forthcoming publication. Parameters r and q are then evaluated from molecular-structure data.

Figure 4 shows a few calculated $\tilde{P} - \tilde{v}$ isotherms for different values of parameter c. Figure 4 indicates what is easily verified by inspection of Equation (14): for fixed

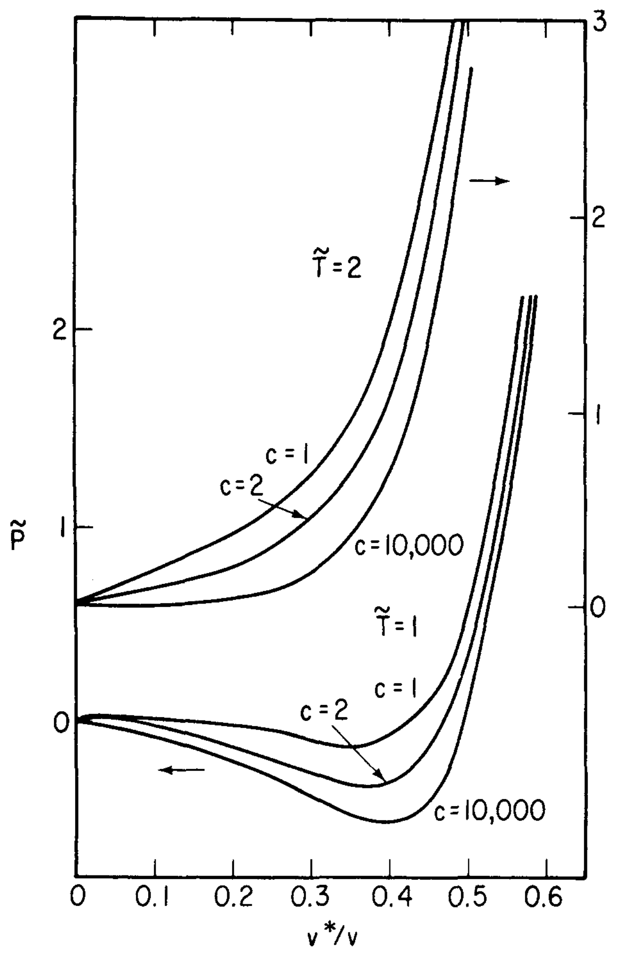


Fig. 4. Effect of parameter c on reduced equation of state. The ratio V*/V is the reduced density.

values of $\tilde{T}$ and $\tilde{v}$, parameter c is of much importance when c is of the order of unity, but its importance rapidly decreases at large values of c.

For argonlike molecules, as c, r, and q all $\rightarrow 1$, Equation (14) reduces to the perturbed–hard-sphere result of Alder (Alder et al., 1972). In that event we have a two-parameter, corresponding-states equation of the form

$$\tilde{P} = f(\tilde{v}, \tilde{T}) \tag{18}$$

For polymers, as $1/c \rightarrow 0$, Equation (14) reduces to the form suggested by Prigogine (1957), also a corresponding-states equation:

$$\tilde{P} = f(\tilde{v}, \tilde{T}) \tag{19}$$

In Equations (18) and (19) the functions f are not the same, although they are closely related as shown in Equation (14).

For intermediate values of c, Equation (14) gives a three-parameter, corresponding-states equation:

$$\tilde{P} = f(\tilde{v}, \tilde{T}, c) \tag{20}$$

The second virial coefficient is given by a simple expression shown in Table 1.

The vapor pressure of a liquid is found by equating the chemical potential of the vapor to that of the liquid; the result is also shown in Table 1. Finally, this table also gives expressions for fugacity, residual enthalpy, and residual entropy.

TABLE 2. CHARACTERISTIC PARAMETERS FOR TWENTY TWO FLUIDS AND THREE POLYMERS

	v^*_{sp} cm³/g*	$\left(\frac{\epsilon q}{k}\right)$ °K	c
Methane	1.2361	152.2	1.00
Ethane	0.9077	299.9	1.38
Propane	0.8620	375.0	1.44
Hexane	0.7561	631.4	1.91
n-heptane	0.7414	728.2	2.14
n-dodecane	0.7334	1,045.6	2.58
n-hexadecane	0.7030	1,487.0	3.78
n-eicosane	0.6902	1,808.1	4.46
Ethylene	0.9254	248.4	1.15
i-butane	0.8909	406.3	1.38
Benzene	0.6042	605.2	1.54
Cyclohexane	0.6625	620.7	1.66
Hydrogen	3.6034	24.3	1.00
Argon	0.3777	119.6	1.00
Nitrogen	0.6438	102.3	1.00
Carbon monoxide	0.6549	107.1	1.00
Carbon dioxide	0.4031	315.1	1.46
Hydrogen sulfide	0.5505	358.0	1.32
Sulfur dioxide	0.3476	478.6	1.61
Water	0.5357	818.3	1.87
9(2-phenylethyl)heptadecane	0.6490	1,986.5	4.52
1,7-dicyclopentyl-4(3-cyclopentylpropyl)heptane	0.6309	1,945.1	4.18

* $M_w v^*_{sp} = rv^*$, where M_w = molecular weight.

For polyethylene $T^* = \frac{\epsilon q}{kc} = 474.7$°K, $P^* = \frac{\epsilon q}{rv^*} = 1{,}229$ bars, $v^*_{sp} = 0.6563$ cm³/g.

For polyisobutylene $T^* = 472.7$°K, $P^* = 1{,}782$ bars, $v^*_{sp} = 0.6012$ cm³/g.

For polystyrene $T^* = 544.0$°K, $P^* = 1{,}691$ bars, $v^*_{sp} = 0.5316$ cm³/g.

DATA REDUCTION

The three adjustable parameters ($\epsilon q/k$), rv^*, and c can be obtained from *PVT* data for gases and liquids and from vapor-pressure data. We have obtained these parameters for twenty-two pure fluids and for several polymers; results are given in Table 2. Since our ultimate aim is to use the new equation of state for calculation of phase equilibria (K factors) and enthalpies for mixtures, we used primarily vapor pressures and *PVT* data for liquids. For very large molecules (polymers), only *PVT* data were used.

Figures 5 and 6 show some calculated and observed vapor pressures, and Table 3 gives a measure of deviations between calculated and observed vapor pressures. Figure 7 shows some calculated and observed saturated liquid densities, and Figure 8 compares predicted with observed second virial coefficients. Table 4 shows experimental and predicted enthalpies for methane, isobutane, nitrogen and water; results are given for both gases and liquids.

For all properties agreement is good, although improvement in second virial coefficients is desirable. What is more gratifying, the results indicate that Equation (14) is applicable to a wide variety of fluids, from hydrogen to eicosane to polyethylene.

While the effect on vapor pressures is small, allowing parameter rv^* to be slightly temperature-dependent improves agreement between calculated and observed enthalpies and liquid densities. Because of methane's special importance in technology, temperature-dependent rv^* parameters were evaluated for methane as given in the Appendix.

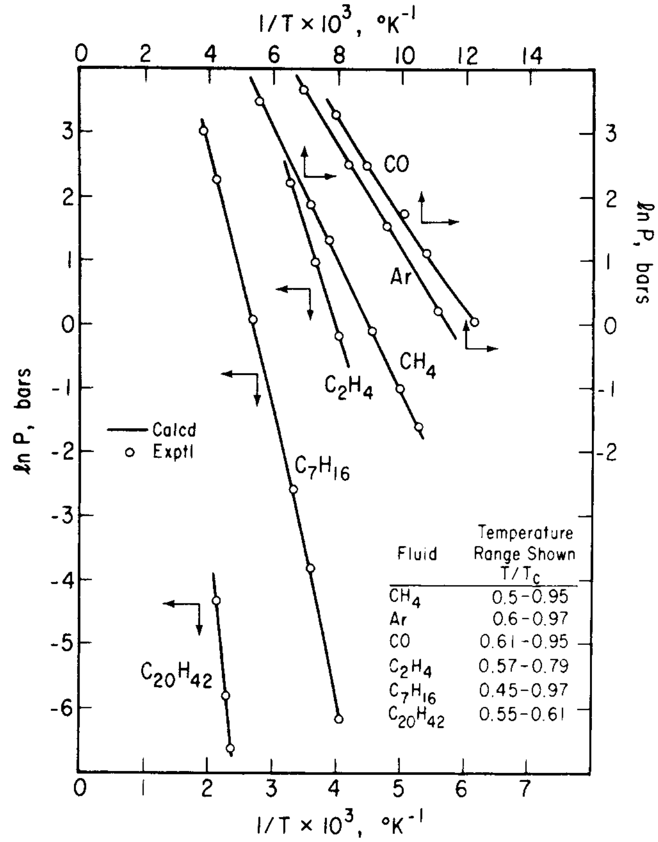


Fig. 5. Calculated and experimental vapor pressures for six nonpolar fluids.

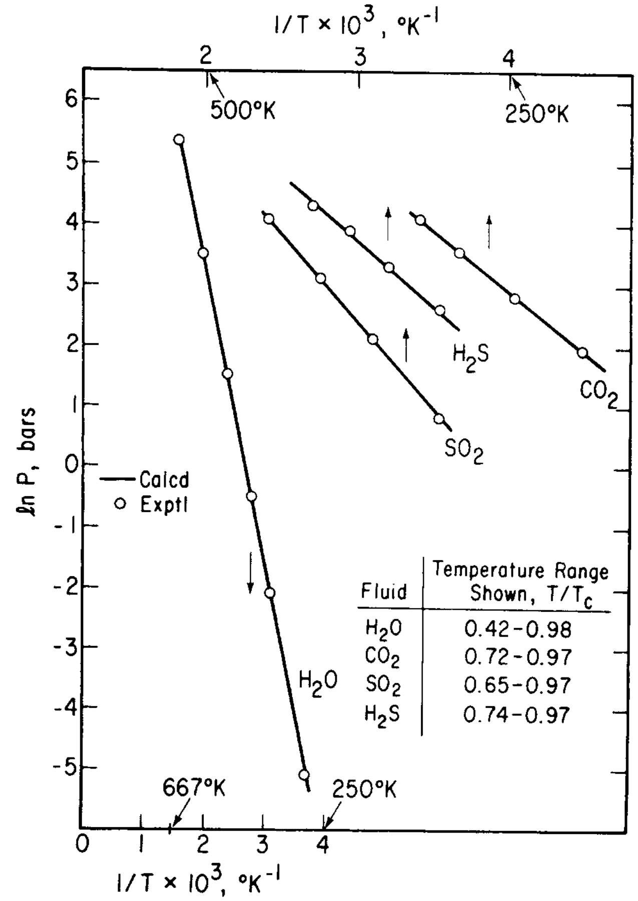


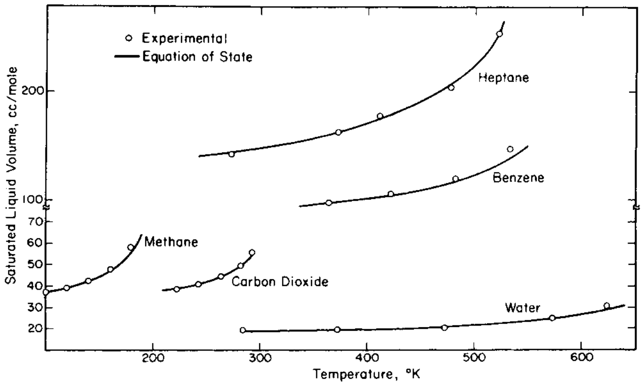
Fig. 6. Calculated and observed vapor pressures for carbon dioxide and three polar fluids.

TABLE 3. ROOT-MEAN-SQUARE AND MAXIMUM DEVIATIONS IN VAPOR PRESSURE

	Temperature range T/T_c	Root-mean-square deviation %*	Maximum deviation %
Methane	0.53-0.99	1.0	1.7
i-butane	0.71-0.96	0.47	0.8
Benzene	0.55-0.97	2.6	4.8
Dodecane	0.57-0.64	0.39	1.1
Water	0.72-0.98	3.4	5.2
Sulfur dioxide	0.66-0.96	1.33	2.9
Carbon dioxide	0.73-0.96	0.6	1.0

* Root-mean-square deviation $= \left\{ \frac{1}{n} \sum_{i=1}^{n} \left(\frac{\Delta P}{P} \times 100 \right)^2 \right\}^{1/2}$

where n is the number of experimental data points.



CALCULATED AND OBSERVED SATURATED LIQUID VOLUMES

Fig. 7. Calculated and observed saturated liquid volumes.

As shown in Figure 9, parameters rv^* are closely related to van der Waals volumes V_w calculated from the group-contribution method of Bondi (1968). Similarly, as shown in Table 5, parameters ϵq are closely related to the energy of vaporization E_o, as defined by Bondi, and as calculated by a group-contribution method (Bondi, 1968).

Figure 9 and Table 5 indicate that Bondi's group-contribution tables may be useful for calculating parameters for Equation (14) for large molecules where experimental data are scarce.

CRITICAL REGION

The new equation of state presented here [Equation (14)] is a three-parameter equation. If parameter c is fixed, we can solve for the critical constants using the relations

$$(\partial P/\partial V)_T = 0 \quad \text{and} \quad (\partial^2 P/\partial V^2)_T = 0$$

at the critical point. We performed the differentiations numerically, and Table 6 shows results for a few values of c. The critical compressibility factors are too large, al-

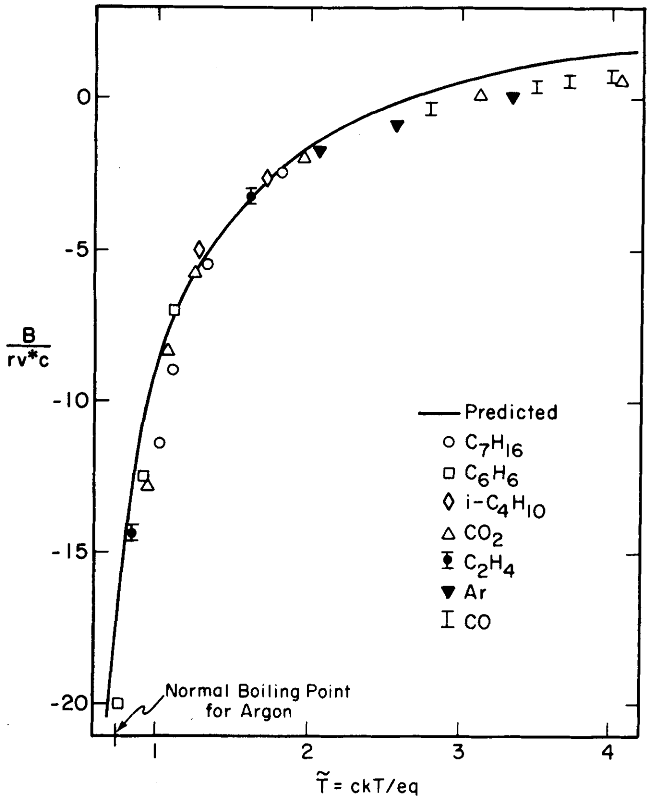


Fig. 8. Predicted (not fitted) second-virial coefficients. All parameters obtained from data at high densities.

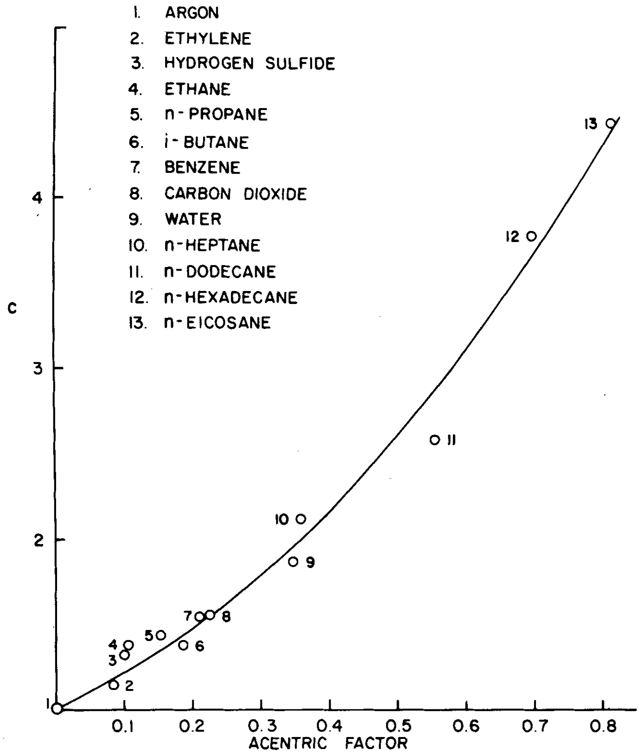


Fig. 10. For small and intermediate sized molecules, the number of external degrees of freedom 3c is related to the acentric factor.

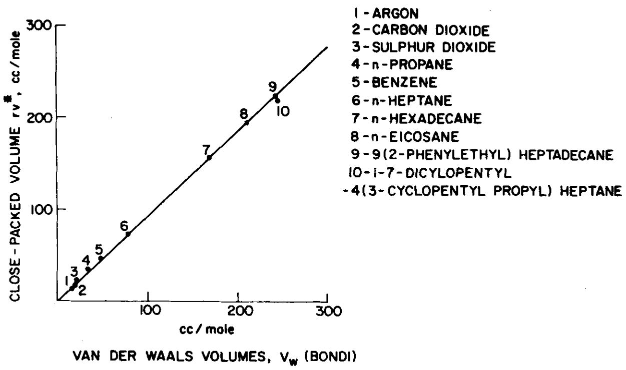


Fig. 9. Correlation of close-packed volumes with Bondi's van der Waals volumes.

TABLE 4. RESIDUAL ENTHALPIES FOR METHANE, ISOBUTANE, NITROGEN, AND WATER AT REPRESENTATIVE TEMPERATURES AND PRESSURES

Fluid	Temp. °K	Pressure bars	— Residual enthalpy kcal/mole Experimental	Calculated
Methane†	120	55.4	1.91	1.88 *
		274.8	1.78	1.76 *
	160	153.1	1.64	1.67 *
	250	99.6	0.63	0.61
	300	150.6	0.57	0.56
		211.7	0.73	0.72
Isobutane**	420	176.0	3.57	3.62
		321.0	3.52	3.56
	500	30.5	0.61	0.59
		294.0	2.84	2.99
	600	39.6	0.45	0.50
		148.5	1.58	1.65
Nitrogen††	66.7	74.1	1.38	1.29 *
	72.2	146.7	1.30	1.23 *
	94.4	275.2	1.11	1.10 *
	138.9	36.0	0.31	0.30
	166.7	73.1	0.40	0.39
	222.2	155.8	0.36	0.36
Water***	323.2	223.7	10.2	10.0 *
	373.2	245.1	9.69	9.74 *
	473.2	253.0	8.68	8.99 *
	773.2	68.0	0.33	0.29
	973.2	88.0	0.23	0.23
		214.0	0.57	0.56

* Liquid phase.
† Goodwin, 1974.
** API, Project 44, 1953.
†† Jacopsen et al., 1973.
*** East, 1964.

though they decrease with rising c, in agreement with experiment. It is now well established (Rowlinson, 1972; Levelt-Sengers, 1974) that all analytical equations of state are poor in the critical region; Equation (14) is no exception. Results based on molecular dynamics are also poor in the critical region because they depend strongly on the number of particles included in the computer simulation. For reliable results in the critical region, it is necessary to perform computer calculations with a very large number of particles, requiring computers larger than those now available.

For normal fluids (as defined by Lewis, Pitzer, et al., 1961) we expect that c correlates well with the acentric factor ω. Such a correlation is shown in Figure 10.

TABLE 5. RELATION BETWEEN CHARACTERISTIC PARAMETER ϵq AND BONDI'S E_0

	ϵq	E_0	$100\,\epsilon q/E_0$
	cal/mole		
Methane	302	2,000	15
Ethane	596	3,940	15
n-propane	745	5,290	14
n-heptane	1,446	9,540	15
n-dodecane	2,077	14,980	14
n-hexadecane	2,953	19,260	15
n-eicosane	3,591	23,540	15
Ethylene	493	3,490	13
i-butane	807	6,200	13
Nitrogen	203	1,318	15
Benzene	1,202	7,270	16
Water	1,623	9,000	18
Sulfur dioxide	958	5,455	17

TABLE 6. REDUCED CRITICAL CONSTANTS AND THE CRITICAL COMPRESSIBILITY FACTOR*

c	$\tilde{v}_c$	$\tilde{T}_c$	$\tilde{P}_c$	z_c
1	4.725	1.317	0.101	0.364
1.5	5.330	1.488	0.066	0.356
2	5.796	1.602	0.408	0.346
3	6.579	1.751	0.029	0.327
10	12.316	2.123	0.005	0.313

* $\tilde{v}_c = \dfrac{V_c}{Nrv^*}$ $\quad \tilde{T}_c = \dfrac{ckT_c}{\epsilon q}$

$\tilde{P}_c = \dfrac{P_c r v^*}{\epsilon q}$ $\quad z_c = \dfrac{\tilde{P}_c \tilde{v}_c c}{T_c}$

BRIEF COMPARISON WITH OTHER THREE-PARAMETER EQUATIONS OF STATE

Numerous empirical or semiempirical three-parameter equations have been proposed. One that has recently received much attention is a modified Redlich-Kwong equation (Soave, 1972).

The original Redlich-Kwong equation was intended only for gases, not for liquids (Redlich and Kwong, 1949). The Redlich-Kwong equation (and its many modifications) is fundamentally not suited for liquids because, if the temperature is low or the pressure is high (or both), the term $v - b$ becomes negative and the equation of state yields meaningless results. (The function a is always positive.) This limitation, also present in the original van der Waals equation, was recognized by van der Waals and his co-workers many years ago. Equation (14) does not suffer from this deficiency because for all fluid densities the reduced density $\tilde{v}^{-1}$ is always less than unity.

As shown by Soave (1972), a modified Redlich-Kwong equation can be used successfully to represent vapor-pressure data. However, when the adjustable parameters are fitted to do so, the calculated liquid densities are in poor agreement with experiment. Equation (14) does not suffer from this deficiency. More important, however, Equation (14), unlike other three-parameter equations of state, is applicable to fluids containing very large molecules as well as to those containing simple molecules.

ACKNOWLEDGMENT

The authors are grateful to the Gas Processors' Association, The American Petroleum Institute, the American Gas Association, and the National Science Foundation for financial support; to the Computer Center, University of California, Berkeley, for the use of its facilities; and to E. R. Bazúa for helpful discussions.

NOTATION

A_{nm} = dimensionless constants in Equation (14) given in the Appendix
B = second virial coefficient
$3c$ = number of external degrees of freedom per molecule
d = hard-sphere diameter
E_o = Bondi's energy of vaporization
f = fugacity
f = a function
H = enthalpy
k = Boltzmann's constant
M_w = molecular weight
N = number of molecules
P = pressure
Q = canonical partition function
$q_{r,v}$ = contribution to partition function arising from rotational and vibrational degrees of freedom
r = number of segments per molecule
R = gas constant
S = entropy
T = temperature
V = total volume of the system of N molecules
V_f = free volume
v = volume per mole
ω = acentric factor
ϕ = potential field
ϵq = characteristic energy per molecule
τ = a constant equal to 0.7405

Superscripts

R = residual property
L = liquid state
G = gaseous state
$*$ = reducing property
$\sim$ = reduced property

Subscripts

c = critical property
int = internal (independent of density)
ext = external (dependent on density)
n = index (an integer) in Equation (17) for the exponent in a Taylor series in reciprocal reduced temperature
m = index (an integer) in Equation (17) for the exponent in a Taylor series in reciprocal reduced volume

LITERATURE CITED

Alder, B. J., D. A. Young, and M. A. Mark, "Studies in Molecular Dynamics," *J. Chem. Phys.*, **56**, 3013 (1972).

American Petroleum Institute, Research Report 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press (1953).

Bender, E., "An Equation of State for Predicting Vapor-Liquid Equilibria of the System N_2-Ar-O_2," *Cryogenics*, **13**, 11 (1973).

Bondi, A., *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York (1968).

Carnahan, N. F., and K. E. Starling, "Intermolecular Repulsions and the Equation of State for Fluids," *AIChE J.*, **18**, 1184 (1972).

East, K., "National Engineering Laboratory Steam Tables", H. M. Stationary Office, Edinburgh, Scotland (1964).

Flory, P. J., "Thermodynamics of Polymer Solutions," *Disc. Faraday Soc.*, **49**, 7 (1970).

Goodwin, R. D., "Thermophysical Properties of Methane, from 90 to 500°K at Pressures to 700 bars," *NBS Tech. Note* 653 (1974).

Gosman, A. L., R. D. McCarthy, and J. G. Hust, "Thermodynamic Properties of Argon From the Triple Point to 300°K at Pressures to 1000 atm.," National Standard Reference Data Series (NBS), No. 27 (1969).

Hijmans, J., "Phenomenological Formulations of the Principle of Corresponding States for Liquids Consisting of Chain Molecules," *Physica*, **27**, 433 (1961).

Hill, T. L., *Introduction to Statistical Thermodynamics*, p. 286, Addison-Wesley, Reading, Mass. (1962).

Jacopsen, R. T., R. B. Stewart, R. D. McCarty, and H. J. M. Hanley, "Thermophysical Properties of Nitrogen From the Fusion Line to 3500°R for Pressures to 15000 Psia," NBS Tech. Note 648 (1973).

Levelt-Senger, J. M. H., "From van der Waals Equation to Scaling Laws," *Physica*, **73**, 73 (1974).

Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2 ed., Appendix 1, McGraw-Hill, New York (1961).

Patterson, D., and G. Delmas, "Corresponding States Theories and Liquid Models," *Disc. Faraday Soc.*, **49**, 98 (1970).

Prigogine, I., *The Molecular Theory of Solutions*, North Holland Publishing Co., Amsterdam (1957).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions V," *Chem. Rev.*, **44**, 233 (1949).

Reed, T. M., and K. E. Gubbins, *Applied Statistical Mechanics*, McGraw-Hill, New York (1973).

Rowlinson, J. S., "The Thermodynamics of the Critical Point in One-Component Systems," *Ber. Bunsen-Ges. Phys. Chem.*, **76**, 281 (1972).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Vera, H. J., and J. M. Prausnitz, "Interpretative Review. Generalized van der Waals Theory for Dense Fluids," *Chem. Eng. J.*, 3, 1 (1972).

Manuscript received April 23, 1975; revision received June 27, and accepted July 8, 1975.

APPENDIX

The molecular-dynamic results of Alder are given in a form where the Holmholtz energy is the sum of a hard-sphere part and a perturbation part; the latter follows from attractive intermolecular forces. These are represented by a square-well potential where the width of the well is a fixed multiple (½) of the hard-sphere diameter. For the hard-sphere part we use the Carnahan-Starling equation. For the perturbation part we use Alder's results:

$$W(\tilde{T}, \tilde{v}) = \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{A_{nm}}{\tilde{v}^m} \right) \left(\frac{1}{\tilde{T}^{n-1}} \right) \tag{A1}$$

The dimensionless constants A_{nm} are

$A_{11} = -7.0346$
$A_{12} = -7.2736$
$A_{13} = -1.2520$
$A_{14} = 6.0825$
$A_{15} = 6.8$
$A_{16} = 1.7$

$A_{21} = -0.33015580 \times 10^1$
$A_{22} = -0.98155782 \times 10^0$
$A_{23} = +0.22022115 \times 10^3$
$A_{24} = -0.19121478 \times 10^4$
$A_{25} = +0.86413158 \times 10^4$
$A_{26} = -0.22911464 \times 10^5$
$A_{27} = +0.35388809 \times 10^5$
$A_{28} = -0.29353643 \times 10^5$
$A_{29} = +0.10090478 \times 10^5$

$A_{31} = -0.11868777 \times 10^1$
$A_{32} = +0.72447507 \times 10^1$
$A_{33} = -0.17432407 \times 10^2$
$A_{34} = +0.19666211 \times 10^2$
$A_{35} = -0.85145188 \times 10^1$

$A_{41} = -0.51739049 \times 10^0$
$A_{42} = +0.25259812 \times 10^1$
$A_{43} = -0.41246808 \times 10^1$
$A_{44} = +0.23434564 \times 10^1$

When

$n = 1, \quad M = 6$
$n = 2, \quad M = 9$
$n = 3, \quad M = 5$
$n = 4, \quad M = 4$

For methane the effect of temperature on v^*_{sp} is given by

$$v^*_{sp} = 1.467662 - 1.504333\tilde{T} + 2.695236\tilde{T}^2 - 2.046844\tilde{T}^3 + 0.8062849\tilde{T}^4 - 0.1735586\tilde{T}^5 + 0.019398\tilde{T}^6 - 0.0008816\tilde{T}^7$$

where subscript *sp* (specific) indicates that v^* is per gram.

The Decomposition Kinetics of Molybdenite in an Argon Plasma

R. J. MUNZ and W. H. GAUVIN
McGill University, Montreal, Quebec, Canada

A reactor system was developed for the study of heterogeneous reaction kinetics in plasma tail flames. This system was used to investigate the thermal decomposition kinetics of stationary particles of molybdenum disulfide in both the molten and solid state when exposed to argon flames in the temperature range 3 000°K to 8 000°K.

In the solid state a shrinking-core reaction model was obeyed. The rate of reaction was largely controlled by the diffusion of sulfur vapor outwards through the product layer. An apparent activation energy of 134

R. J. Munz is with Noranda Research Centre, Pointe-Claire, Quebec, Canada.