Cubic Equations of State

Limitations and capabilities of a generic cubic equation of state are analyzed in light of observed real-fluid behavior, and criteria are presented for classification of specializations of the generic equation. An example is worked out which illustrates the application of these criteria to the development of new equations of state.

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SCOPE

Since the work of van der Waals a century ago, more than 100 new fluid-phase thermal equations of state have been proposed. Because of the stringent demands for representation of modern high-precision data and of the needs of engineers for ever more versatile design tools, complexity is a dominant feature of the newer equations of state. Given the availability of electronic computers, complexity is of course no longer a severe disadvantage, but there nevertheless remain incentives for the study of equations of state of relatively simple algebraic form containing only a few adjustable parameters. Such equations still enjoy wide use for engineering screening studies and as research tools for semiquantitative prediction or rationalization of equilibrium phenomena. Moreover, the simpler expressions are commonly employed as bases for the development of more comprehensive equations of state. Effective use of a simple equation in any of these capacities clearly requires an understanding of its limitations and capabilities.

The best known simple equations of state are cubic in volume; most of them are specializations of the generic equation

$$P = \frac{RT}{V - b} - \frac{\theta}{V^2 + \delta V + \epsilon}$$

where b, δ, and ϵ are constants for a given fluid, and θ is an arbitrary function of temperature. Many of these specializations give quite reasonable representations of the gross features of real-fluid PVT behavior, but each of them suffers certain shortcomings. Attempts at relieving these shortcomings by direct means (that is, by modifying existing equations so as to obtain new expressions of the same generic type) have met with only limited success. A common failing of all cubic equations proposed to date is their inability, when constrained to satisfy the classical derivative conditions on the critical isotherm, to provide simultaneously acceptable predictions of the second virial coefficient B, of the critical compressibility factor Z_c, and of high pressure volumetric behavior. In order to determine if this limitation is inherent to cubic equations and, in addition, to ascertain to what extent observed second virial coefficient behavior can be conveniently incorporated into a cubic equation of state, we have undertaken a brief study of the generic cubic equation. Standard methods are employed: a reduced form of the equation is found, and properties of the reduced equation are examined in light of observed real-fluid behavior. Only pure fluids are considered.

CONCLUSIONS AND SIGNIFICANCE

No specialization of the generic cubic equation, when subjected to the classical constraints $(\partial P/\partial V)_{T,c} = (\partial^2 P/\partial V^2)_{T,c} = 0$, can provide both accurate values for B and satisfactory representation of the critical and high-pressure regions. Acceptable prediction of both low- and high-pressure behavior requires at the very least that the critical compressibility factor implied by the equation of state be treated as an empirical parameter different in general from experimental values of Z_c. If parameters b, δ, and ϵ are treated as constants, quantitative representation of both B and C (the third virial coefficient) is impossible, for accurate prediction of B at subcritical temperatures precludes prediction of the observed maximum in C.

One may, however, develop in a straightforward manner simple and compact specializations of the generic equation suitable for accurate work for limited ranges of the state variables. We illustrate the development of such a specialization for low pressures and obtain as a byproduct a simple correlation for the second virial coefficients of normal fluids. For many applications, this correlation is comparable in accuracy to the correlation of Pitzer and Curl.

GENERIC CUBIC EQUATION OF STATE

We consider the equation of state

$$P = \frac{RT}{V - b} - \frac{\theta}{V^2 + \delta V + \epsilon} \qquad (1)$$

where θ is an arbitrary function of temperature, and b, δ, and ϵ are constants for a given fluid. Equation (1) may be viewed as an extension of the van der Waals equation, to which it reduces as the simplest nontrivial special case (θ = const. = a; $\delta = \epsilon = 0$). Partington and Shilling (1924) list about a dozen equations which are specializations of Equation (1); modern examples are due to Redlich and Kwong (1949), Himpan (1951, 1952, 1954), and others.

Application of Equation (1) to a specific fluid requires that numerical values first be determined for the parameters b, δ, ϵ, and any others which enter through the arbitrary temperature function θ. The conventional approach is to impose a few selected mathematical or numerical constraints upon the equation of state and to determine values for the parameters by solution of the system of resulting equations. Practically, the choice of constraints depends upon the number and nature of the equation-of-state parameters to be determined and upon the anticipated application of the equation of state.

Martin and Hou (1955), Martin et al. (1959), and Martin (1967) discuss many of the features of real-fluid behavior which lend themselves to convenient expression as constraints for equation-of-state work. Not all of these features can be incorporated into equations of the type considered here; inclusion of some of them in fact precludes satisfactory representation of others. We shall adopt as two of our constraints the classical conditions

$$(\partial P/\partial V)_{T,c} = 0 \tag{2}$$

$$(\partial^2 P/\partial V^2)_{T,c} = 0 \tag{3}$$

where subscript c denotes the gas-liquid critical state.

Equation (1) may be written

$$V^3 + \left(\delta - b - \frac{RT}{P}\right)V^2 + \left(\epsilon - \delta b - \frac{RT\delta}{P} + \frac{\theta}{P}\right)V - \left(\epsilon b + \frac{RT}{P}\epsilon + \frac{\theta b}{P}\right) = 0 \tag{4}$$

A requirement equivalent to Equations (2) and (3) [Martin and Hou, 1955) is that Equation (4), when specialized to the critical state, has three equal roots, that is, that it be of the form

$$(V - V_c)^3 \equiv V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \tag{5}$$

Setting $T = T_c$ and $P = P_c$ in Equation (4), and comparing the result with Equation (5), we obtain three equations relating the equation-of-state parameters to the critical constants. Solving for the dimensionless parameters $\hat{b}$, $\hat{\delta}$, and $\hat{\epsilon}$, we find

$$\hat{b} = \zeta_c + \Omega_c - 1 \tag{6}$$

$$\hat{\delta} = \Omega_c - 2\zeta_c \tag{7}$$

$$\hat{\epsilon} = \zeta_c^2 - \Omega_c\zeta_c - \Omega_c^2\ (\Omega_c - 1) \tag{8}$$

where Ω_c is the value of the dimensionless temperature function

$$\Omega \equiv (\theta P_c/R^2T_c^2)^{1/3} \tag{9}$$

evaluated at $T = T_c$, and

$$\hat{b} \equiv bP_c/RT_c \tag{10}$$

$$\hat{\delta} \equiv \delta P_c/RT_c \tag{11}$$

$$\hat{\epsilon} \equiv \epsilon P_c^2/R^2T_c^2 \tag{12}$$

$$\zeta_c \equiv P_cV_c/RT_c \tag{13}$$

Anticipating that for many applications the value of ζ_c [either as implied by Equations (2) and (3) or as fixed by the user] may not be equal to the actual critical compressibility factor, we have used the designation ζ_c instead of Z_c. It is understood in all that follows that when $\zeta_c \neq Z_c$, the critical volume V_c is defined by Equation (13).

The generic Equation (1) may now be put in reduced form. Eliminating b, δ, ϵ, and θ in favor of their dimensionless analogues by Equations (9) through (12), and introducing ζ_c and Ω_c via Equations (6), (7), and (8), we find on rearrangement that

$$P_r = \frac{T_r}{\zeta_c(V_r - 1) - (\Omega_c - 1)} - \frac{\Omega^3}{\zeta_c^2(V_r - 1)^2 + \Omega_c\zeta_c(V_r - 1) - \Omega_c^2(\Omega_c - 1)} \tag{14}$$

or alternatively,

$$Z = \frac{\zeta_cV_r}{\zeta_c(V_r - 1) - (\Omega_c - 1)} - \frac{\zeta_c\Omega^3V_r}{T_r[\zeta_c^2(V_r - 1)^2 + \Omega_c\zeta_c(V_r - 1) - \Omega_c^2(\Omega_c - 1)]} \tag{15}$$

The variables T_r, P_r, and V_r are the dimensionless quantities T/T_c, P/P_c, and VP_c/ζ_cRT_c, respectively, and Z is the compressibility factor. Equation (14) satisfies the reduced forms of the derivative conditions (2) and (3) for any ζ_c and for any reduced temperature function Ω.

Equation (15) can be expressed in the virial form

$$Z = 1 + \frac{\hat{B}}{\zeta_cV_r} + \frac{\hat{C}}{(\zeta_cV_r)^2} + \cdots \tag{16}$$

where $\hat{B}$, $\hat{C}$, etc. are reduced second, third, etc. virial coefficients, related to the corresponding dimensional quantities by

$$\hat{B} \equiv BP_c/RT_c$$

$$\hat{C} \equiv CP_c^2/R^2T_c^2$$

etc.

Employing standard techniques, we expand the right-hand side of Equation (15) in inverse powers of the group ζ_cV_r and find on comparison of the result with Equation (16) that

$$\hat{B} = \zeta_c + \Omega_c - 1 - \frac{\Omega^3}{T_r} \tag{17}$$

$$\hat{C} = (\zeta_c + \Omega_c - 1)^2 + (\Omega_c - 2\zeta_c)\frac{\Omega^3}{T_r} \tag{18}$$

etc.

These expressions, particularly Equation (17), are useful for testing the predictive capabilities of specializations of Equation (1) in the low-to-moderate pressure range. Alternatively, they may be used as guides in the construction of new equations of state of the generic type considered here.

Expressions for derived properties (fugacity coefficient, residual functions, etc.), applicable to specializations of Equation (1) constrained so as to satisfy Equations (2) and (3), are readily obtained from Equation (14) or (15). Although we do not consider these properties in the present discussion, formulae for several of them are given in the Appendix.

SPECIALIZATIONS OF THE GENERIC EQUATION

In order to apply Equation (14) to the calculation of thermodynamic properties, one must first specify (or determine) both ζ_c and the temperature function Ω. For the classical two-constant equations of state (in which δ and ϵ are specified functions of b, and θ contains only a single constant a), Equations (6) (7), and (8) admit direct solution for $\hat{b}$, Ω_c, and ζ_c. Thus for such equations, Ω_c and

ζ_c are not adjustable parameters.

Specializations of Equation (1) with three or more constants allow treatment of ζ_c or of both ζ_c and Ω_c as adjustable parameters to be specified by the user. For these equations, subject only to the constraints of Equations (2) and (3), the most one can generally determine about other parameters buried in Ω is their combined contribution to the critical value Ω_c. Separate determination of these buried parameters requires the imposition of other types of constraints as discussed below.

It is tempting to identify ζ_c with the critical compressibility factor Z_c. However, if one requires precise descriptions of high- and low-pressure behavior, such a procedure is undesirable; this is best illustrated by a simple numerical example. We choose as a class of substances the simple fluids (Ar, Kr, Xe), for which $Z_c \sim 0.291$. From generalized charts we find that $\hat{b}$ (interpreted as a limiting value as $P_r \rightarrow \infty$ of the product $Z_c V_r$) is of the order of 1/10. Equation (6) then gives $\Omega_c = 0.808$, from which by Equation (17) the computed critical value of $\hat{B}$ is $\hat{B}_c = -0.428$. But this value is much too negative; experiment shows that $\hat{B}_c$ is very nearly $-1/3$. Turning the argument around, letting $\hat{B}_c = -1/3$ and $\zeta_c = Z_c = 0.291$, one finds $\Omega_c = 0.649$ and hence $\hat{b} = -0.060$. This latter result is unsatisfactory, as it leads to predictions of negative values of Z at sufficiently high P_r. We conclude that simultaneous quantitative description of both the high-pressure and low-pressure regions is impossible for any specialization of Equation (1), if the equation is required to satisfy Equations (2) and (3), and if experimental values of Z_c are used for ζ_c. This conclusion holds also if b, δ, and ϵ are considered functions of temperature.

As noted above, additional constraints are needed for complete determination of the function Ω if it contains more than a single adjustable parameter. One possible constraint, applicable for $T_r > 1$, is

$$(\partial P_r/\partial T_r)_{V_r=1} = \text{constant} \tag{19}$$

where the constant is in general different for different fluids. Equation (19) expresses the observed linearity of the critical isochore (Martin and Hou, 1955). Another useful relationship (a property of analytic equations of state) is

$$(\partial P_r/\partial T_r)_{V_{r,c}} \equiv (dP_r^{\text{sat}}/dT_r)_c \tag{20}$$

Equation (20) asserts the identity of the slopes of the critical isochore and of the vapor-liquid saturation curve at $T_r = 1$.

Differentiation of Equation (14) with respect to T_r and specialization to $V_r = 1$ yields

$$(\partial P_r/\partial T_r)_{V_r=1} = \frac{(d\Omega^3/dT_r) - \Omega_c^2}{\Omega_c^2(\Omega_c - 1)} \tag{21}$$

The only functional dependence of Ω on T_r compatible with Equation (19) is thus

$$\Omega^3 = \Omega_c^3 + \beta(T_r - 1) \tag{22}$$

with β and Ω_c constant for a given fluid. However, such a function is incompatible with observed second-virial coefficient behavior, for substitution of Equation (22) into Equation (17) gives

$$\hat{B} = \zeta_c + \Omega_c - 1 - \beta + (\beta - \Omega_c^3)T_r^{-1} \tag{23}$$

Equation (23) predicts that $\hat{B}$ varies as T_r^{-1}, while it is known that an optimal single temperature exponent is generally in the range of $-3/2$ to -2. We must therefore concede the inappropriateness of specializations of Equation (14) for simultaneous accurate representation of second virial coefficients and of the critical isochore.

Application of Equation (20) facilitates the introduction of so-called "third (corresponding states) parameters" into specializations of Equation (14). Riedel's parameter α_c, defined as

$$\alpha_c \equiv \left(\frac{d \ln P_r^{\text{sat}}}{d \ln T_r}\right)_c = \left(\frac{dP_r^{\text{sat}}}{dT_r}\right)_c \tag{24}$$

is well suited to this purpose for Equation (20) requires that α_c be numerically equal to the slope of the critical isochore, a quantity which is readily computed for pressure-explicit equations of state. In view of the preceding discussion reasonable expressions for Ω may not yield linear critical isochores; for such cases, however, one may still require that α_c be equal to the slope of the predicted critical isochore at $T_r = 1$. Accordingly, we define an apparent Riedel parameter A_c:

$$A_c \equiv \frac{(d\Omega^3/dT_r)_c - \Omega_c^2}{\Omega_c^2(\Omega_c - 1)} \tag{25}$$

This definition merely represents a specialization of Equation (21) to $T_r = 1$. As with the parameter ζ_c, the choice of notation avoids general identification of A_c with its experimental counterpart α_c. Many specializations of Equation (1) yield universal values for A_c which do not fall in the commonly-encountered range of observed α_c-values (about 5 to 10).

Another corresponding-states parameter which enjoys wide use is Pitzer's acentric factor ω. Empirically, ω for normal fluids is approximately related to α_c by Reid and Sherwood (1966)

$$\alpha_c = \frac{29}{5} + \frac{49}{10}\omega \tag{26}$$

If A_c is identified with α_c, Equations (25) and (26) permit introduction of ω into specializations of Equation (1) through the parameters which appear in the function Ω.

Some popular specializations of Equation (1) are classified in Table 1 on the basis of their values for Ω_c, ζ_c, and A_c. Also shown are the corresponding equations for Ω^3 and for the reduced second virial coefficient $\hat{B}$.

AN APPLICATION

No cubic equation of state can provide precise descriptions of real-fluid behavior in all regions of interest. However, the material of the preceding sections provides a convenient basis for systematic development of simple equations suitable for use over limited ranges of the variables of state. We present here a short example to illustrate the application of this material to the construction of an equation for the low-to-moderate pressure region where the primary requirement is accurate prediction of $\hat{B}$ and $\hat{C}$ and their temperature derivatives.

We proceed by assuming, as a flexible generalization of the classical Ω functions, an expression due to Battelli (1892):

$$\Omega^3 = MT_r^m + NT_r^n \tag{27}$$

For simplicity, Ω_c, ζ_c, m, and n are taken as constants (to be determined), the same for all fluids. Specialization of Equation (27) to $T_r = 1$ and elimination of M yields

$$\Omega^3 = \Omega_c^3\, T_r^m + N\,(T_r^n - T_r^m)$$

from which, according to Equation (25),

TABLE 1. CHARACTERISTICS OF SOME SPECIALIZATIONS OF EQUATION (1)

Equation	Ω_c	$\zeta_c^{(1)}$	$A_c^{(2)}$	Ω^3	$\hat{B}$
van der Waals(3)	3/4	3/8	4	$\frac{27}{64}$	$\frac{1}{8} - \frac{27}{64} T_r^{-1}$
Clausius(4)	3/4	Z_c	7	$\frac{27}{64} T_r$	$Z_c - \frac{1}{8} - \frac{27}{64} T_r^{-2}$
Berthelot(5)	3/4	3/8	7	$\frac{27}{64} T_r$	$\frac{1}{8} - \frac{27}{64} T_r^{-2}$
Redlich & Kwong(6)	$\frac{2^{1/3}+1}{3}$ $\equiv$ 0.7533	1/3	$\frac{7+2^{1/3}}{2(2-2^{1/3})}$ $\equiv$ 5.580	$\frac{(2^{1/3}+1)^3}{27} T_r^{-1/2}$ $\equiv$ $0.4275\, T_r^{-1/2}$	$\frac{2^{1/3}-1}{3} - \frac{(2^{1/3}+1)^3}{27} T_r^{-3/2}$ $\equiv$ $0.0866 - 0.4275\, T_r^{-3/2}$

(1) For real fluids, $Z_c \sim 0.2 - 0.3$.

(2) For real fluids, $\alpha_c \sim 5 - 10$.

(3) $P = \frac{RT}{V-b} - \frac{a}{V^2}$.

(4) $P = \frac{RT}{V-b} - \frac{a}{T(V+c)^2}$.

(5) $P = \frac{RT}{V-b} - \frac{a}{TV^2}$.

(6) $P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$.

$$A_c = \frac{\Omega_c^2(m\Omega_c - 1) + N(n-m)}{\Omega_c^2(\Omega_c - 1)}$$

The acentric factor ω is introduced by forcing identity of this expression with Equation (26). It follows that

$$m = \frac{29\Omega_c - 24}{5\Omega_c}$$

$$N = \frac{49\Omega_c^3(\Omega_c - 1)\omega}{48 + (10n - 58)\Omega_c}$$

It is convenient at this point to specify Ω_c and ζ_c. The choices $\Omega_c = 3/4$ and $\zeta_c = 1/3$ yield acceptable values for both $\hat{b}$ and $\hat{B}$ (1/12 and −65/192, respectively), and moreover lead to a particularly simple form of the reduced equation of state, for the denominator of the second term in Equation (14) reduces to a simple square if $\Omega_c = 3/4$. The expressions for m and N thus become

$$m = -3/5$$

$$N = -\frac{441\omega}{128(5n+3)}$$

Of the four parameters in Equation (27), all but one (n) have been eliminated. This remaining parameter is fixed by consideration of $\hat{B}$. The expression for $\hat{B}$ implied by Equations (17) and (27), with parameters given as above, is

$$\hat{B} = B^0 + \omega B^1 \tag{28a}$$

where

$$B^0 \equiv \frac{1}{12} - \frac{27}{64} T_r^{-8/5} \tag{28b}$$

$$B^1 \equiv \frac{441}{128(5n+3)} (T_r^{n-1} - T_r^{-8/5}) \tag{28c}$$

In writing Equations (28), we have borrowed the notation of Pitzer and Curl (1957), as the present expression for $\hat{B}$ is similar in form to their correlation of second virial coefficient data.

The function B^0, which contains no undetermined parameters, must represent the reduced second virial coefficients of simple fluids, for which $\omega = 0$. In Figure 1, a plot of Equation (28b) superimposed upon $\hat{B}$ data for Ar, Kr, and Xe illustrates that this is indeed a valid interpretation of B^0. Agreement between Equation (28b) and the data is excellent over the range $T_r = 0.6$ to 3.0. Also shown on Figure 1 is the Pitzer-Curl B^0 correlation. Except for very high and low T_r, the two correlations are essentially the same.

We may now determine a value for n by analysis of $\hat{B}$ data for non-simple ($\omega \neq 0$) fluids. On Figure 2 is shown a plot of such data for 16 compounds, reduced to values of B^1(exp), where

$$B^1(\text{exp}) \equiv \frac{1}{\omega} [\hat{B}(\text{exp}) - B^0]$$

The notation(exp) denotes experimental values, and B^0 is defined by Equation (28b). The data for $\hat{B}$(exp), taken from the compilation of Dymond and Smith (1969), are for fluids having values of ω which range from 0.123 (CS_2) to 0.398 (n-octane). An acceptable fit of the B^1(exp) values is obtained from Equation (28c) with $n = -13/5$. Overall agreement with experiment is comparable to that for the Pitzer-Curl correlation for B^1 (the dashed line on Figure 2). The temperature derivatives of B^1 are more sensitive to the form of the correlation and are less easily compared with experiment. However, both correlations yield similar values of dB^1/dT_r for $T_r < 1$ and hence will give comparable values for the usual derived properties at subcritical temperatures.

The expression for Ω is now completely determined, and we can write down the final form of the equation of state. Equation (27) becomes

$$\Omega^3 = \frac{27}{64} T_r^{-3/5} + \frac{441}{1280} \omega (T_r^{-13/5} - T_r^{-3/5})$$

and Equation (14) specializes to

$$P_r = \frac{12T_r}{4V_r - 1} - \frac{81/20\,[(60 - 49\omega)T_r^{-3/5} + 49\omega\, T_r^{-13/5}]}{(8V_r + 1)^2} \qquad (29)$$

with

$$V_r \equiv \frac{3P_cV}{RT_c}$$

Equation (29) is a three-parameter reduced equation of state, with corresponding-states parameters T_c, P_c, and ω.

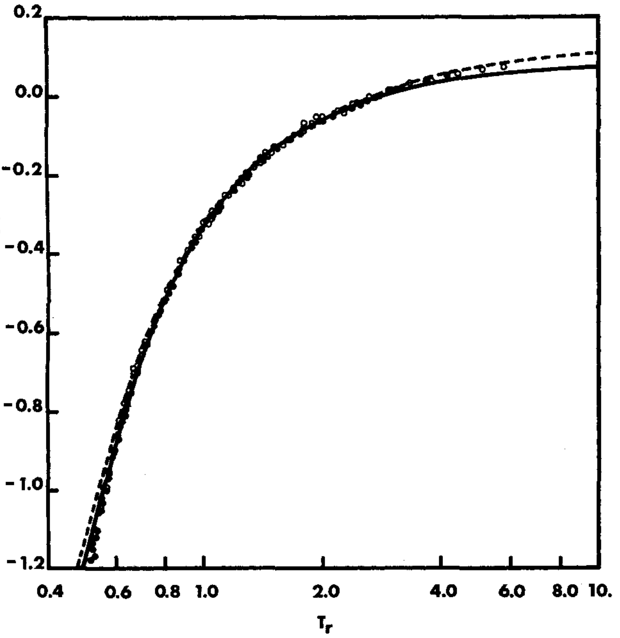

Fig. 1. $\hat{B}$ vs. T_r for simple fluids. Symbols are data for Ar, Kr, and Xe. Solid line is Equation (28b); dashed line is the Pitzer-Curl correlation for B^0.

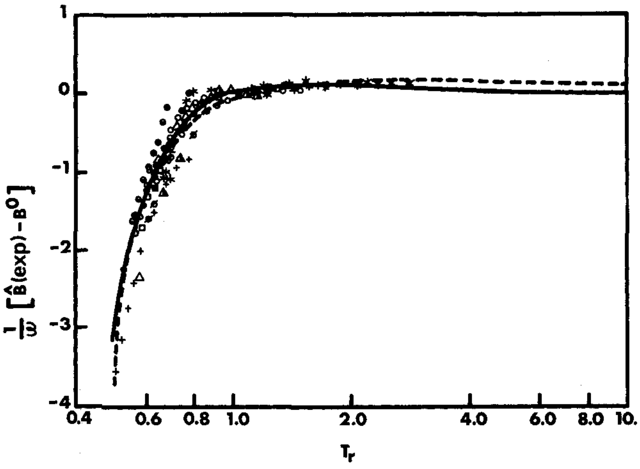

Fig. 2. $\frac{1}{\omega}$ $[\hat{B}(\text{exp})-B^0]$ vs. T_r for nonsimple fluids. Symbols are data for 16 fluids: CS_2, propylene, propane, iso-butane, 1-butene, neo-pentane, *n*-butane, cyclohexane, benzene, iso-pentane, CO_2, *n*-pentane, SO_2, *n*-hexane, *n*-heptane, *n*-octane. Solid line is Equation (28c) with $n = -13/5$; dashed line is the Pitzer-Curl correlation for B^1.

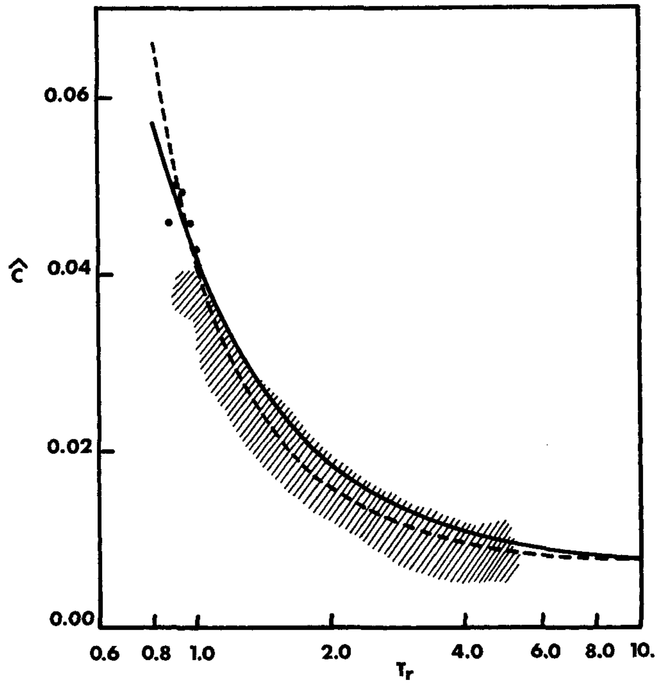

Fig. 3. $\hat{C}$ vs. T_r for several fluids. Shaded area indicates spread of data for Ar, Kr, Xe, N_2 and CH_4. Points are for *n*-octane. Lines are Equation (30) with $\omega = 0$ (solid) and with $\omega = 0.398$ (dashed).

It is instructive to examine the third-virial-coefficient behavior implied by Equation (29). Equation (18) specializes to

$$\hat{C} = C^0 + \omega C^1 \qquad (30a)$$

where

$$C^0 \equiv \frac{1}{144} + \frac{9}{256} T_r^{-8/5} \qquad (30b)$$

$$C^1 \equiv \frac{147}{5120} (T_r^{-18/5} - T_r^{-8/5}) \qquad (30c)$$

Reliable third virial coefficient data are scarce. The shaded area on Figure 3 represents the spread of $\hat{C}$ data compiled by Dymond and Smith (1969) for Ar, Kr, Xe, N_2, and CH_4 (substances having small or zero ω); the five points are for *n*-octane ($\omega = 0.398$). Shown for comparison are curves calculated from Equation (30) with $\omega = 0$ and with $\omega = 0.398$.

Equation (30) provides a qualitative correlation of $\hat{C}$ for simple fluids for $T_r \geqq 1$, and the predicted dependence of $\hat{C}$ on ω, although surely incorrect in detail, is sufficiently weak to preclude gross error when $T_r > 1$. However, both experiment and statistical-mechanical calculations indicate that $\hat{C}$ exhibits a maximum at about $T_r = 0.9$, a phenomenon not represented by Equation (30). The inability to predict this behavior is not unique to Equation (30) but results from an implied relationship between $\hat{B}$ and $\hat{C}$ common to all specializations of Equation (1) for which b, δ, and ϵ are treated as constants. Thus, by Equations (17) and (18),

$$\hat{C} = (\zeta_c + \Omega_c - 1)(2\Omega_c - \zeta_c - 1) - (\Omega_c - 2\zeta_c)\hat{B}$$

according to which an extremum in $\hat{B}$ implies an extremum in $\hat{C}$ at the same T_r, provided that $\Omega_c \neq 2\zeta_c$. Since no extremum occurs in $\hat{B}$ for $T_r \sim 0.9$, accurate representation of $\hat{B}$ precludes even qualitative correlation of $\hat{C}$ below this temperature level. For T_r below about 0.8 or 0.9, however, the impact of an inaccurate $\hat{C}$ is minimal, as the maximum density at which a fluid can exist as a vapor is small.

Because of the good correlation for $\hat{B}$, and the reasonable (but not precise) predictions for $\hat{C}$, the useful range of Equation (29) probably extends to about $V_r = 1$. Accurate description of the critical isochore is impossible with Equation (29), since Ω^3 is not linear in T_r, and predictions for V_r much less than unity are likely to be in error because of the emphasis given the low-pressure region in building the equation.

Further refinements to the approach illustrated here are possible. For example, one can treat parameters b, δ, and ϵ as functions of temperature, and develop cubic equations which yield more realistic expressions for $\hat{C}$. Another, perhaps less desirable, possibility is to relax one or both of the critical-derivative constraints [Equations (2) and (3)], and thereby gain some additional flexibility. This approach may generate regions of spurious thermodynamic instability.

Full use of material presented earlier led to Equation (29), developed from the reduced version of Equation (1) as given by Equation (14). One might instead proceed from a particular form of Equation (14) corresponding to a cubic equation of known capabilities. The Redlich and Kwong equation is a logical choice, and modification of the temperature function Ω of the original Redlich and Kwong equation leads to new equations of the type proposed by Wilson (1964) and by Barner et al. (1966).

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NOTATION

A_c = apparent Riedel parameter; see Equation (25)
B = second virial coefficient
b = parameter in Equation (1)
C = third virial coefficient
$\Delta H'$ = residual enthalpy $\equiv H$ (ideal gas) $- H$
P = pressure
R = gas constant
$\Delta S'$ = residual entropy $\equiv S$ (ideal gas) $- S$
T = absolute temperature
V = molar volume
Z = compressibility factor $\equiv PV/RT$
α_c = Riedel's parameter
δ = parameter in Equation (1)
ϵ = parameter in Equation (1)
ζ_c = apparent critical compressibility factor
θ = arbitrary temperature function in Equation (1)
φ = fugacity coefficient
Ω = reduced temperature function; see Equation (9)
ω = Pitzer's acentric factor

Subscripts

c = critical state
r = reduced value of T, P, or V

Superscripts

0 = simple-fluid contribution to $\hat{B}$ or $\hat{C}$
1 = non simple-fluid contribution to $\hat{B}$ or $\hat{C}$
$\wedge$ = dimensionless (reduced) quantity
sat = saturation state of pure fluid

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APPENDIX. DERIVED PROPERTIES

Application of standard formulas to Equation (15) yields the following expressions for the fugacity coefficient and the residual enthalpy and entropy:

$$\ln \varphi = Z - 1 - \ln Z + \ln \frac{\zeta_c V_r}{\zeta_c V_r - (\zeta_c + \Omega_c - 1)} - \frac{\Omega^3}{T_r} I(V_r) \qquad \text{(A1)}$$

$$\frac{\Delta H'}{RT} = 1 - Z + \frac{\Omega^3 - T_r(d\Omega^3/dT_r)}{T_r} I(V_r) \qquad \text{(A2)}$$

$$\frac{\Delta S'}{R} = \frac{\Delta H'}{RT} + \ln \varphi \qquad \text{(A3)}$$

with Z given by Equation (15) and the function $I(V_r)$ defined as follows:

for $\Omega_c < 3/4$,

$$I(V_r) \equiv \frac{2}{\Omega_c\sqrt{3 - 4\Omega_c}} \left[\frac{\pi}{2} - \tan^{-1} \frac{2\zeta_c(V_r - 1) + \Omega_c}{\Omega_c\sqrt{3 - 4\Omega_c}} \right] \qquad \text{(A4a)}$$

for $\Omega_c = 3/4$,

$$I(V_r) \equiv \frac{8}{8\zeta_c(V_r - 1) + 3} \qquad \text{(A4b)}$$

for $\Omega_c > 3/4$,

$$I(V_r) \equiv \frac{1}{\Omega_c\sqrt{4\Omega_c - 3}} \ln \frac{2\zeta_c(V_r - 1) + \Omega_c + \Omega_c\sqrt{4\Omega_c - 3}}{2\zeta_c(V_r - 1) + \Omega_c - \Omega_c\sqrt{4\Omega_c - 3}} \qquad \text{(A4c)}$$

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