The experimental data are usually between the values predicted by the van Laar and the Wilson equations. Thus, it may be advisable to average these equations for some critical design problems.

The van Laar constants A and B and the Wilson constants A_{12} and A_{21} are presented in Table II for the different pressures investigated. The constants reported by Wilson and Simons (2) are also shown in this table. The data of these authors are used to calculate the van Laar and the Wilson parameters by means of the "Gradient Search Optimization" program. The results of these computations are presented in Table II.

A noticeable difference in the values of the van Laar and the Wilson parameters is observed. This is more significant for Wilson than van Laar parameters. The reasons for such a discrepancy may be explained as follows: The criteria used for the approach to the minimum by various authors and the different programs do not coincide. It appears that the objective function has a rather flat minimum; therefore, a rather wide range of parameters for the van Laar and Wilson equations can be obtained to fit the experimental data.

The nature of the objective function which has been considered by different authors will affect the best values of the constants of the van Laar and Wilson equations.

The range of experimental data to which the equations are fitted also has some effect on the values of the constants.

Acknowledgment

The computer time made available by Pahlavi University's computer center is acknowledged.

Nomenclature

p_i° = vapor pressure of component i, mm Hg absolute
x_i = mole fraction of isopropanol in liquid phase
y_i = mole fraction of isopropanol in vapor phase
γ_i = activity coefficient of component i
π = total pressure, mm Hg absolute

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Received for review February 21, 1973. Accepted June 4, 1973.

Application of Hard Sphere Equation of State to Real Fluids

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Several variations of an equation of state formed by combining a hard sphere term with an attractive term are tested by comparison with *PVT* data for gaseous argon, six alkanes, tetrafluoromethane, and perfluorocyclobutane. The parameters are evaluated by a nonlinear regression calculation, and the two best equations are described in detail. Both fit well up to near the critical density and hold for nonspherical molecules as well as for spherical molecules. The equation with the attractive term derived from the Barker-Henderson theory is better than the van der Waals approximation. However, it is still not suitable for precise correlations above the critical density.

A few years ago, Reiss et al. (*11*) and Thiele (*14*) derived the following equation of state of the classical hard sphere fluid:

$$P/(\rho kT) = \Phi_1(y) = (1 + y + y^2)/(1 - y)^3 \qquad (1)$$

where

$$y = \tfrac{1}{6}\pi\sigma^3\rho \qquad (2)$$

and where $\rho = N/V$ is the number density, and σ is the diameter of the spheres.

Equation 1 reproduces closely the exact virial series obtained from molecular dynamics experiments of Alder and Wainwright (*11*) up to the fourth virial coefficient.

Carnahan and Starling (*2*) noted that the numerical coefficients of the virial series are close to the integral numbers,

$$P/(\rho kT) = 1 + 4y + 10y^2 + 18y^3 + 28y^4 + 40y^5 + \ldots \qquad (3)$$

and, therefore, the series can be expressed by

$$P/(\rho kT) = \Phi_2(y) = (1 + y + y^2 - y^3)/(1 - y)^3 \qquad (4)$$

The seventh virial coefficient resulting from this treatment agrees with the value calculated by Ree and Hoover (*10*). Hence, $\Phi_2(y)$ may be expected to be valid up to the densities corresponding to the liquid state.

To demonstrate the application of the hard sphere equation of state, modified to allow for intermolecular attraction, to the correlation of the thermodynamic properties of fluids, a series of equations obtained by combining the two functions from Equations 1 and 4 with various types of attractive terms has been tested by comparison of the observed and calculated compressibility factors for nine gases over a wide range of temperature and pressure. These gases contain molecules of various sizes and shapes but exhibit weak intermolecular forces. The "observed" data for argon and the hydrocarbons have already been smoothed, but we feel that they represent the real values accurately. The parameters were evaluated by a nonlinear least-squares method, and the root-mean-square deviations, as well as individual deviations, were examined and compared for the different equations. The results for the two best equations are given below.

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Van der Waals-Type Attractive Term

The term owing to intermolecular attraction was first derived by van der Waals in the general form $\rho a/(kT)$, where a is a characteristic parameter. More recently, Kac et al. (*6*) showed this form to be exact in the case of weak intermolecular forces. Hence, we may write:

$$PV/(RT) = \Phi(y) - a(T)/(RTV) \qquad (5a)$$

where V is the molar volume, $\Phi(y)$ is either $\Phi_1(y)$ or $\Phi_2(y)$, and

$$y = b(T)/V \qquad (5b)$$

where $a(T)$ and $b(T)$ are temperature-dependent parameters.

Rogers and Prausnitz (*12*) recently demonstrated that Equation 5 with $\Phi(y)$ given by the equation of Carnahan and Starling, $\Phi_2(y)$, and $a(T)/V$ obtained from the theory of Barker and Henderson (*1*) yields good agreement with the experimental compressibility data for argon, methane, and neopentane in the critical region and even at liquid densities. In these calculations, σ in Equation 2 is replaced by the effective collision diameter, σ_e, defined by Barker and Henderson (*1*) by the expression:

$$\sigma_e = \int_0^{\sigma} \left[1 - \exp\left(\frac{-u(r)}{kT}\right)\right] dr \qquad (6)$$

where $u(r)$ is the intermolecular energy at distances $r \leq \sigma$ and was expressed by Rogers and Prausnitz by means of the Kihara potential.

The adequacy of Equation 5 has never been tested in the calculation of the compressibilities of nonspherical molecules. In this case, σ would represent a certain average diameter, but the question remains whether the equation is suitable to the same extent as it is for spherical molecules.

If the first term, $\Phi(y)$, is exact, the equation offers a way to test the usual assumption that there is a simple relation between σ (or σ_e) and the critical volume V^c of a fluid. Furthermore, it allows one to obtain realistic values of the second term, $a(T)/V$, from the compressibility data of a gas and to test it independently in various ways, for example, comparison with the configurational energy of a liquid as in Table III.

Initial calculations have shown that $b(T)$ varies with the temperature and that the variation approximately conforms to that of the cube of σ_e, given by Equation 6. The integration is greatly simplified by the use of the three-step potential (*8*). The three-step potential differs from the two-step potential (*7*) in that in addition to the two steps of attraction, there is a step of repulsion whose height is equal to the depth of the attraction step, $\bar{u}/k$. Thus, in the range $0 < r \leq \sigma$ we have

$$u(r)/k = \infty \text{ for } 0 < r < (\sigma - s_1^*)$$

$$u(r)/k = -\bar{u}/k = 1.43\, T^c (V^*/V_o^*)^{1/3} \qquad (7)$$

$$\text{for } (\sigma - s_1^*) < r \leq \sigma$$

where T^c is the critical temperature (in K), V^* is the *liquid* molar volume at the reduced temperature $T/T^c = 0.6$, and V_o^* is that of a reference substance, methane (*1*), for which $(V_o^*)^{1/3} = 3.375\ (\text{cm}^3\ \text{mol}^{-1})^{1/3}$.

An approximate value of the range s_1^*, obtained from the data on the second virial coefficients (*8*), is $s_1^* = 0.112\,\sigma$ and, therefore,

$$\sigma_e = \sigma\left[1 - 0.112 \exp\left(\frac{\bar{u}}{kT}\right)\right]$$

and

$$b(T) = b_\infty \left[1.126 - 0.126 \exp\left(\frac{\bar{u}}{kT}\right)\right]^3 \qquad (8)$$

where b_∞ is the limiting value of $b(T)$ when $T \rightarrow \infty$.

These relations imply that upon collisions at high temperatures, the molecules undergo a deformation such that the diameter along the collision axis becomes instantaneously about 11% smaller than that of the molecules at rest. The numerical coefficients in Equation 8 are the most suitable average values for hydrocarbons. For fluorocarbons s_1^* is smaller, and $b(T)$ depends on the temperature to a lesser extent. Nevertheless, Relation 8 was used for both "soft" and "hard" molecules.

The variation of the second parameter, $a(T)$, with the temperature depends on at least two factors: the temperature dependence of the radial distribution function and that of orientation-dependent intermolecular forces (*13*). The two effects combined may be expressed by the relation

$$a(T)/R = (a'/R)[1 + c'/(RT)] \qquad (9)$$

where a' and c' are constants.

The constants b_∞, a', and c' were evaluated by a nonlinear regression procedure from compressibility data over wide temperature and pressure ranges indicated in Table I. For argon the smoothed data given by Gosman et al. (*5*) and obtained mostly from the measurements of Michels and coworkers were used. For the gaseous alkanes the new, improved smoothed data given in the j-tables of the API Research Project 44 were chosen. For the two fluorocarbons the experimental data of Douslin et al. (*3, 4*) were used. For all the substances except CF_4, the lowest PV isotherm chosen for evaluation of the constants was that determined just above T^c.

The constants were evaluated for the two hard sphere compressibility terms, $\Phi_1(y)$ and $\Phi_2(y)$. The results obtained for the Carnahan-Starling equation, $\Phi_2(y)$, were somewhat better and are reported in Table I.

The most important result of these calculations is that the root-mean-square (rms) deviations are almost the same for spherical or quasispherical molecules as for nonspherical molecules. The deviations are the smallest for CF_4 because the data used were determined at temperatures remote from T^c (227.6K). The errors in the calculated values are the largest in the critical region; and invariably for all the substances, the isotherm calculated just above T^c exhibits an S-shape, characteristic for liquid-vapor equilibrium. The van der Waals approximation for $a(T)$ does not suffice in this region.

Barker and Henderson Theory

The attractive term can be evaluated more accurately from the Helmholtz energy expression given by Barker and Henderson [the "macroscopic compressibility approximation" (*1*)]:

$$\frac{A - A_h}{NkT} = \frac{2\pi\rho}{kT}\int_0^\infty u(r) g_h(r) r^2 dr - \frac{\pi\rho}{kT}\left(\frac{\partial\rho}{\partial P}\right)_h \int_\sigma^\infty u^2(r) g_h(r) r^2 dr \qquad (10)$$

where the subscript "*h*" refers to the functions for hard spheres.

Since $(\partial\rho/\partial P)_h$ becomes small at high densities, it may be evaluated from $\Phi_1(y)$ [instead of $\Phi_2(y)$]:

$$(\partial\rho/\partial P)_h = (1 - y)^4 (1 + 2y)^{-2} (kT)^{-1} \qquad (11)$$

The compressibility factor is given by

$$\frac{P}{\rho kT} = \Phi_2(y) + \rho \frac{\partial}{\partial \rho}\left[\frac{A - A_h}{NkT}\right]_T \tag{12}$$

Owing to Equation 11, the second term in Equation 10 is of the second order in $1/(kT)$. We have found, however, that it does not suffice to account for the temperature dependence of $P/(\rho kT)$ and we assumed that $u(r)$ is generally a function of temperature; empirically the first term in Equation 10 was expressed by

$$-4(a/RT)[1 + c/(RT)]y$$

It was assumed that $g_h(r)$ *is equal to unity at all values of* r *and* ρ. Therefore, the constants of the equation of state was evaluated from experimental data at pressures not exceeding 200 atm.

The semiempirical forms are (per mole)

$$\frac{A - A_h}{RT} = -\frac{4a}{RT}\left(1 + \frac{c}{RT}\right)y - 2\left(\frac{d}{RT}\right)^2 \left(1 + \frac{c}{RT}\right)^2 \frac{y(1-y)^4}{(1+2y)^2} \tag{13}$$

and from Equation 12,

$$\frac{PV}{RT} = \Phi_2(y) - \frac{4a}{RT}\left(1 + \frac{c}{RT}\right)y - 2\left(\frac{d}{RT}\right)^2\left(1 + \frac{c}{RT}\right)^2 \frac{y(1-y)^4}{(1+2y)^2} \cdot \left[1 - \frac{4y}{(1-y)} - \frac{4y}{(1+2y)}\right] \tag{14}$$

where a, c, and d are constants. The values of the constants obtained by using the same experimental data (at pressures up to 200 atm) are given in Table II.

The rms deviations are smaller than those given in Table I (except for neopentane), partly because of a smaller pressure range of the experimental data but also because of some improvement of the calculated values in the critical region. Nevertheless, Equation 14 still gives isotherms which have slight S-shaped characters at the critical temperature and a few degrees above the critical temperature.

The results are greatly improved when the constants of Equation 14 are fitted to the *PVT* data at densities *not exceeding* the critical density. The values of (d/R) and the relative importance of the second term in Equation 13 then become larger than the values given in Table II [the value of (d/R) also depends strongly on the choice of b_∞]. The equation holds also at and near the critical density but fails at high densities and at all temperatures. The errors at high densities are not larger than in the values calculated from the Benedict-Webb-Rubin equation. The BWR equation was compared with the experimental data for perfluorocyclobutane determined by Douslin et al. (*4*).

The results of our calculations confirm the assumption that there exists a simple relation between σ_e and V^c or V^*. The ratios b^*/V^* and b^c/V^c, where b^* and b^c are the values of $b(T)$ at $T = 0.6\ T^c$ and $T = T^c$, respectively, are approximately constant. The value of $b(T)$ at $T = 0$ is equal to 1.428 b_∞ (Equation 8) and is close to b^*. Consequently, $b_{(T=0)}/V^*$ is also approximately constant and

$$b_\infty/V^* \approx 0.290 \pm 0.004$$

This relation is useful only for an initial estimation of b_∞ because the compressibilities are (unfortunately) sensitive to the value of b_∞.

Although the equation of state, Equation 14, does not reproduce well the density dependence of $P/(\rho kT)$ at high densities, it conforms well to the temperature dependence of the compressibility factor. Therefore, we may attempt to evaluate the internal energy from the thermodynamic relation,

$$\frac{U - U_h}{NkT} = -T\frac{\partial}{\partial T}\left[\frac{A - A_h}{NkT}\right]$$

and to compare it with the observed values for the liquid at $T = 0.6\ T^c$ and $V = V^*$ (the liquid molar volume at this temperature). Neglecting the second-order term in $(A - A_h)$, which must be negligible at high densities, we obtain

$$\frac{U - U_h}{RT} \approx -\frac{4ay}{RT}\left(1 + \frac{2c}{RT}\right) + \frac{4a}{R}\left(\frac{\partial y}{\partial T}\right)_v\left(1 + \frac{c}{RT}\right) \tag{15}$$

where $(\partial y/\partial T)_v$ is obtained from Equation 8.

Mansoori et al. (*9*) recently derived accurate relations for mixtures of hard spheres. The relation for $(A_h - A_{id})$, where A_{id} is the free energy of a perfect gas, is

$$(A_h - A_{id})/(RT) = -3 + 2(1-y)^{-1} + (1-y)^{-2} \tag{16}$$

and, therefore,

$$(U_h - U_{id})/(RT) = -2\,T(\partial y/\partial T)_v[(1-y)^{-2} + (1-y)^{-3}] \tag{17}$$

The residual (configurational) energy, which is equal to that of the system minus that of a perfect gas at the same temperature (*13*), is

$$U^* = (U - U_h) + (U_h - U_{id})$$

Table I. Constants of Equation 5 for $\Phi(y) = \Phi_2(y)$

Substance	Range of experimental data		a'/R, K cm^{-3} mol	c'/R, K	b_∞, cm^3 mol^{-1}	rms dev
	Temp, K	Pressure, atm				
Argon[a]	151–300	0.1–600	1.566×10^4	28.92	8.515	0.0141
Methane[b]	180–600	1–700	2.760	34.44	11.49	0.0283
Ethane[b]	306–600	1–500	5.528	127.2	16.73	0.0282
Propane[b]	370–600	1–700	9.266	164.9	23.17	0.0336
n-Butane[b]	426–550	1–300	12.33	209.0	28.08	0.0228
Isobutane[b]	410–550	1–300	11.86	209.7	28.52	0.0217
Neopentane[b]	436–550	1–200	15.35	211.4	34.20	0.0217
Tetrafluoromethane[c]	273–623	15–390	2.800	230.6	15.97	0.0093
Perfluorocyclobutane[d]	388–623	17–395	10.21	440.5	36.31	0.0356

[a] Gosman et al. (*5*). [b] Zwolinski et al. (*15*). [c] Douslin et al. (*3*). [d] Rowlinson (*13*).

Table II. Constants of Equation 14

Substance	a/R, K	c/R, K	$(d/R)^2$, K_2	b_∞, cm^3 mol^{-1}	rms dev
Argon	413.3	1.848	5.82×10^3	8.26	0.0078
Methane	508.7	7.470	10.9	10.79	0.0070
Ethane	727.2	55.97	34.1	15.5	0.0114
Propane	832.4	95.16	20.9	21.8	0.0104
n-Butane	943.8	116.0	42.7	27.3	0.0142
Isobutane	886.3	122.8	31.15	27.8	0.0151
Neopentane	949.6	123.3	7.39(?)	34.1	0.0217
Tetrafluoromethane	433.6	115.1	2.71	15.7	0.0063
Perfluorocyclobutane	628.3	283.4	2.81(?)	35.1	0.0204

Table III. Comparison of Observed and Calculated Residual Energies U* of Liquids at $T = 0.6\ T^c$

Substance	$\frac{U^*/(RT)}{\text{Observed}}$	$\frac{(U - U_h)/(RT)}{\text{Equation 15}}$	$\frac{(U_h - U_{id})/(RT)}{\text{Equation 17}}$	$\frac{U^*_{calc}}{U_{obs}}$
Argon	−7.65	−8.03	0.46	0.988
Methane	−7.72	−8.36	0.41	1.03
Ethane	−8.69	−10.58	0.35	1.18
Propane	−9.54	−11.89	0.33	1.21
n-Butane	−10.0	−11.97	0.28	1.17
Isobutane	−9.89	−12.35	0.28	1.22
Neopentane	−10.1	−12.25	0.25	1.19
Tetrafluoromethane	−9.77	−14.60	0.40	1.45
Perfluorocyclobutane	(−12.2)[a]	−16.31	0.27	1.31

[a] Uncertain value.

The two terms evaluated at $T = 0.6\ T^c$ and $V = V^*$ are compared in Table III with the observed values (*8*). The ratios of calculated to observed values are close to unity only for argon and methane. For the remaining compounds, the calculated values of $-U^*$ are too low. A plausible explanation is that, owing to a restricted rotation in the liquid phase, $(A - A_h)$ depends on the temperature less than in the gas, and the appropriate constant c/R is smaller than the value obtained from gas compressibilities. In other words, the temperature dependent part of $u(r)$ is much less noticeable in a liquid than in a moderately compressed gas.

Conclusions

We thus propose two equations for the practical correlation of *PVT* data and related properties of fluids of weakly interacting molecules. These are Equations 5a, along with the auxiliary relations 5b, 8, and 9, and Equation 14. Both equations are grounded in modern statistical theories of equilibrium properties of matter. The parameters have a direct interpretation in terms of the properties of the molecules and of the forces between them. They can be evaluated either with *PVT* data alone or with the help of critical constants, liquid volume, and energy of vaporization.

Equation 5a is a relatively simple function containing three empirical parameters. It is quite accurate up to near the critical density, and it is suitable for many purposes at even higher densities. Equation 14 is more complicated and contains four parameters. It is more accurate at higher densities and gives better derivatives of compressibility with respect to temperature and pressure than Equation 5a.

Nomenclature

P = pressure, atm
V = volume (molar), $cm^3\ mol^{-1}$
T = temperature, K
A = Helmholtz energy
U = energy (internal)
R = gas constant, 82.0562 cm^3 atm $K^{-1}\ mol^{-1}$
N = number of molecules
ρ = number density, N/V
r = intermolecular distance
σ = collision diameter of a molecule (at rest)
σ_e = effective collision diameter of a molecule
$u(r)$ = intermolecular energy
$\bar{u}/k$ = minimum value of $u(r)$ (divided by the Boltzmann constant
T^c, P^c, V^c = liquid-vapor critical constants
$a(T)$, $b(T)$ = temperature-dependent parameters
b^*, b^c, b_∞ = values of $b(T)$ at $T = 0.6\ T^c$, $T = T^c$, and $T = \infty$, respectively

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Received for review February 26, 1973. Accepted July 9, 1973. Work supported in part by the API Research Project 44 of the Thermodynamics Research Center, Texas A&M University and by the Texas A&M Engineering Experiment Station.