Intermolecular Repulsions and the Equation of State for Fluids

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This investigation demonstrates the advantages of an improved expression for intermolecular repulsions in equations of state. A highly accurate equation of state for the rigid-sphere fluid is used as the model of repulsion behavior in real fluids. A method for general usage of this new rigid-sphere equation in real fluid models is presented via reformulation of van der Waal's equation using the accurate new rigid-sphere equation to describe repulsion effects. To test this reformulation, properties of methane, ethane, propane, n-butane, isobutane, hydrogen sulfide, nitrogen, ethylene, acetylene, methyl chloride, cyclohexane, pentane and octane have been calculated. The advantage of using the accurate rigid-sphere equation was demonstrated by the general improvement in calculated properties relative to the original van der Waals and Redlich-Kwong equations. Calculations of enthalpy departures for mixtures of nitrogen and methane, propane and methane, pentane and cyclohexane, and pentane and octane also indicated the desirability of using the accurate rigid-sphere equation to describe repulsion effects in mixtures.

PURE FLUIDS

Since van der Waals (*1*) proposed his theoretical model of the equation of state in 1873, the development of improved analytical models of the equation of state has proceeded along two routes, empirical and theoretical. Indeed, some empirical models have been based, in part, upon theoretical forms.

The totally empirical models of the equation of state are generally employed to correlate experimental thermodynamic property data. They are, therefore, quite accurate in making interpolative calculations of the data from which they have been evaluated. Such evaluations are usually made by regression techniques requiring a considerable amount of experimental data to minimize errors in interpolative calculations. These equations of state generally are specific to a given material. They usually are not easily generalized (*2*) such that accurate calculations can be made for a material not included in the original correlation.

On the other hand, theoretical or semitheoretical equations of state do not require vast amounts of experimental data for their evaluation. Using only a few characteristic bits of experimental data (for example, critical pressure, critical temperature, critical compressibility factor, latent heat of vaporization at the normal boiling point, etc.), these equations allow predictive calculations of properties at other temperatures and pressures. Such calculations naturally lack the accuracy of the regression-spawned equations of state. Yet, for calculating the properties of materials for which reliable experimental data are scarce, the theoretical and semitheoretical equations are definitely useful.

Theoretical equations of state usually are developed using virial expansion theory (*2*), distribution function theory (*2*), or some form of cell model or free volume theory (*3*). A number of theoretical equation of state formulations utilize the molecular model of rigid spheres with long range attractions (and perhaps soft repulsions). This leads to a rigid-sphere repulsion term, plus something else which generally accounts for cohesion effects. Such a model corresponds to the general form of the van der Waals equation

$$P = P_R + P_A \tag{1}$$

Subscript R denotes the rigid-sphere repulsion effect, while A denotes the effects of attractions, etc.

The drawback in deriving the rigid-sphere repulsion term from kinetic theory or free-volume theory is that the result is valid only as a low-order approximation. Recall the rigid-sphere equation of Clausius (*4*) (which now is known to be correct only in one dimension)

$$P_R = RT/(V - b) = RT\,\rho/(1 - b\rho) = RT\rho/(1 - 4y) \tag{2}$$

where $y = b\rho/4$. The virial expansion of this equation is

$$P_R = RT\,\rho(\,1 + 4y + 16y^2 + 64y^3 + 256y^4 + \ldots) \tag{3}$$

However, the exact expansion for rigid-spheres is (*5*)

$$P_R = RT\rho(1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + \ldots) \tag{4}$$

So, the Clausius equation is accurate only to the second term in the series. For higher densities, this equation predicts too large a repulsion pressure, unless one treats the constant b as a function of density These difficulties can be overcome by using a more accurate rigid-sphere equation instead of the kinetic theory term. Such an improved equation for rigid-spheres was developed by Carnahan and

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Starling (*6*) in 1969

$$P_R = RT\rho(1 + y + y^2 - y^3)/(1 - y)^3 \qquad (5)$$

This equation has been shown to be the most accurate analytical equation for rigid spheres yet developed (*6*); it has the following virial expansion:

$$P_R = RT\rho(1 + 4y + 10y^2 + 18y^3 + 28y^4 + \ldots) \qquad (6)$$

In the following sections of this paper, the effect of using (5) instead of (2) is examined by making comparative calculations with the original and substituted forms of the van der Waals and Redlich-Kwong equations of state.

Thermodynamic Properties From the Equation of State

Prior to making calculations based upon specific forms of real gas equations, it will be helpful to generalize the method used to derive the equations for the thermodynamic properties relative to an ideal gas at the same temperature and pressure. The so-called "departure properties" are commonly solved for quantities from equation of state methods.

$$P = P_{rs} + \phi(V, T), \qquad (7)$$

where P_{rs} = rigid-sphere pressure, (6)
$\phi(V, T)$ = soft-repulsion and cohesion pressure term [corresponds to P_A of (1)]

Now

$$(dP/dT)_V = (R/V)Z_{rs} + (d\phi/dT)_V, \qquad (8)$$

where Z_{rs} = rigid-sphere compressibility factor, for example, (5).

The type of functions which are of interest, as isothermal deviations from the ideal gas state, are

$$(U - U^0) = \int_\infty^V [T(dP/dT) - P]dV = \int_\infty^V [T(d\phi/dT)]dV \qquad (9)$$

$$(H - H^0) = (U - U^0) + (PV - RT), \qquad (10)$$

$$(S - S^0) = R\int_\infty^V (PV/RT - 1)\, d\ln V + \ln(Z) = (S - S^0)_{rs} + \int_\infty^V (\phi/T)dV + R\ln(Z/Z_{rs}), \qquad (11)$$

$$(G - G^0) = (H - H^0) - T(S - S^0) \qquad (12)$$

$$(A - A^0) = (U - U^0) - T(S - S^0), \qquad (13)$$

$$\ln(f/P) = [Z - 1) - \ln(Z)] - \int_0^\rho \frac{(Z_{rs} - 1)}{\rho}\, d\rho - \int_0^\rho \frac{\phi}{RT\rho^2}\, d\rho \qquad (14)$$

Doing things this way, one can easily discern the changes made in the thermodynamic property relations, derived from an assumed equation for real fluids, by the substitution of different functional forms for $\phi(T, V)$. The rigid-sphere contribution is assumed to be that obtained from (5).

Simple Two-constant Equations of State

In this section, the rigid-sphere Equation (5) is used to replace the kinetic theory type of repulsion term (2) in two popular equations of state. For the purpose of demonstrating the improvement achieved by the substitution, the present study has been limited to simple two-constant models of the equation of state. There is a twofold reason for this:

1. The general effect can be as easily seen with the simple equations as with more complex forms and perhaps more clearly.
2. The algebraic form of the more complex equations of state is somewhat affected by the algebraic form of the repulsion term. Thus, changing the algebraic form of the repulsion term should be followed by some corresponding reformulation of the other terms (that is, soft repulsion and cohesion terms).

In the category of two-constant equations of state, two examples will be considered. The van der Waals equation is

$$P = RT/(V - b) - a/V^2 \qquad (15)$$

If one assumes the first term on the right of the equal sign to be a rigid-sphere term, then the other term gives

$$\phi = -a/V^2 \qquad (16)$$

The other two-constant equation to be considered is the Redlich-Kwong equation (*7*),

$$P = RT/(V - b) - a/[V(V + b)\sqrt{T}] \qquad (17)$$

Following the same assumption about the first term on the right, the second term gives

$$\phi = -a/[V(V + b)\sqrt{T}] \qquad (18)$$

In both the van der Waals and the Redlich-Kwong equations, the repulsion term $RT/(V - b)$ can be replaced by a rigid-sphere pressure term, for example,

$$P_{rs} = RT(1 + y + y^2 - y^3)/V(1 - y)^3 \qquad (19)$$

Thus, the rigid-sphere version of the van der Waals equation is

$$P = RT(1 + y + y^2 - y^3)/V(1 - y)^3 - a/V^2 \qquad (20)$$

Likewise, the rigid-sphere version of the Redlich-Kwong equation is

$$P = RT(1 + y + y^2 - y^3)/V(1 - y)^3 - a/[V(V + b)\sqrt{T}] \qquad (21)$$

Using the format of the preceding section, one can develop equations for the thermodynamic properties based upon the foregoing equations of state. The results are summarized in Tables 1 and 2.

Calculated Enthalpies

Calculations of gas phase enthalpies have been made with the original and the modified van der Waals and Redlich-Kwong equations. The results of these calculations are compared to experimental data and the resulting deviations are summarized in Table 3 for a variety of substances, many of which are polar and/or not spherically symmetric. Without exception, the ability of the equations to predict enthalpy departures is improved with the use of the more accurate rigid-sphere term (5) as the model for repulsion effects. Recall that these two-constant equa-

TABLE 1. DEFINITION OF EQUATION OF STATE CONSTANTS

	VDW	*RSVDW*	*RK*	*RSRK*
b/V_c	1/3	0.5216	0.26	0.3326
Z_c	3/8	0.359	1/3	0.315715
a/RT_cV_c	9/8	1.38	$1.283\sqrt{T_c}$	$1.463\sqrt{T_c}$

TABLE 2. THERMODYNAMIC PROPERTIES FOR THE TWO-CONSTANT EQUATIONS OF STATE

	P	$(H - H^\circ)/RT$	$\ln(f/P)$
VDW	$RT/(v-b) - a/v^2$	$b/(v-b) - 2a/RTv$	$b/(v-b) - 2a/RTv + \ln(Zv/(v-b))$
RSVDW	$RT(1+y+y^2-y^3)/v(1-y)^3 - a/v^2$	$2y(2-y)/(1-y)^3 - 2a/RTv$	$2y(2-y)/(1-y)^3 + \ln(Z_{rs}/Z) - 2a/RTv$
RK	$RT/(v-b) - a/\sqrt{T}v(v+b)$	$b/(v-b) - a/[RT^{1.5}(v+b)] + (a/2RT^{1.5}b)\ln[v/(v+b)]$	$b/(v-b) - a/[RT^{1.5}(v+b)] + \ln[(v+b)/Zv] + (a/2bRT^{1.5})\ln[v/(v+b)]$
RSRK	$RT(1+y+y^2-y^3)/v(1-y)^3 - a/\sqrt{T}v(v+b)$	$2y(2-y)/(1-y)^3 - a[RT^{1.5}(v+b)] + (a/2RT^{1.5}b)\ln[v/(v+b)]$	$y(8+9y-3y^2)/(1-y)^3$ $\ln(Z) - a/[RT^{1.5}(v+b)] + (a/bRT^{1.5})\ln[v/(v+b)]$

TABLE 3. CALCULATED ENTHALPY DEPARTURES
AVERAGE ABSOLUTE DEVIATION, B.t.u./lb.

Equation	N_2	CO_2	C_2H_4	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
VDW	4.63	17.61	7.50	5.93	13.5	35.0	27.2	10.59	16.5
RSVDW	3.16	13.42	5.04	3.80	9.81	14.9	25.3	7.61	11.1
R-K	1.26	6.09	1.99	1.41	5.53	7.79	10.6	4.55	7.5
RSRK	0.58	0.915	1.18	0.96	2.31	2.11	2.96	2.60	3.4

TABLE 4. CALCULATED DENSITIES
AVERAGE ABSOLUTE DEVIATION, %

Equation	N_2	CO_2	H_2S	C_2H_4	*i*-C_5H_{12}	CH_4	C_3H_8	C_4H_{10}	C_5H_{12}
VDW	2.01	7.47	1.79	4.18	5.52	3.89	9.95	2.27	3.59
RSVDW	0.313	5.51	0.95	2.55	3.91	2.72	6.01	1.80	3.05
R-K	0.737	2.64	0.84	1.33	1.42	1.50	3.07	0.91	1.34
RSRK	0.294	1.49	1.15	1.17	1.14	1.63	1.82	0.64	0.95

tions of state are not theoretically intended for polar molecules nor for molecules which do not have spherical symmetry. Nonetheless, the predictions show the anticipated trend favoring the use of the more accurate rigid-sphere term (5). The overall average of the absolute deviations for the calculated enthalpies are

1. VDW .... 10.56 B.t.u./lbM
2. RSVDW .... 7.59 B.t.u./lbM
3. RK .... 3.82 B.t.u./lbM
4. RSRK ...... 1.80 B.t.u./lbM

Calculated Densities

The results of density calculations with the equations of state (15), (20), (17), and (21) are compared to experimental data and the percentage deviations are summarized in Table 4. Anomalies occur for methane and for hydrogen sulfide. Densities calculated for these materials with the rigid-sphere version of van der Waals' equation (RSVDW) are more accurate than those calculated with the original van der Waals' equation (VDW). Yet, for these substances, densities calculated from the original Redlich-Kwong equation (RK) are more accurate than those calculated with the rigid-sphere version (RSRK).

For the other seven materials included in the study, there seems to be a definite improvement in the density calculations resulting from the use of the more accurate rigid-sphere Equation (5) in place of the kinetic theory expression (2). Indeed, the overall average deviations show the improvement quite markedly. The results are

1. VDW 4.495%
2. RSVDW 2.898%
3. RK 1.496%
4. RSRK 1.133%

Calculated Pressures

The ability of the equations to calculate pressure from experimental temperatures and specific volumes is shown for methylchloride in Table 5. Below the critical isotherm (143.7°C for methyl chloride), all four equations of state are roughly equal, with a slight advantage held by the RSRK equation. Along the critical isotherm, the van der Waals (VDW) equation gives very poor results at and above the critical pressure. For pressures above the critical pressure (hence, densities above the critical density), the RSRK equation gives much better prediction than the other equations. At 206.85 atmospheres (roughly four times the critical pressure), the errors in the predicted

TABLE 5. PREDICTION OF METHYL CHLORIDE PRESSURES FROM EXPERIMENTAL TEMPERATURES AND VAPOR SPECIFIC VOLUMES*

°C	P^*, atm.	*VDW*, atm.	*RSVDW*, atm.	*RK*, atm.	*RSRK*, atm.
125.0	6.975	7.063	7.051	7.02	7.006
	20.049	20.629	20.523	20.555	20.132
	30.664	32.017	31.749	31.109	30.814
	39.817	42.215	41.728	40.630	40.124
	40.015	52.848	52.039	50.407	49.649
143.7 Critical isotherm	9.567	9.632	9.616	9.571	9.549
	30.398	31.288	31.123	30.670	30.449
	51.077	53.818	53.421	52.291	51.731
	69.954	251.92	145.77	103.16	83.291
	101.510	936.55	328.59	200.86	125.46
	206.85	4,265.0	666.61	398.17	196.88

* Data of Hsu and McKetta (8).

Table 6. Calculated Fugacities* Average Absolute Deviation, %

Equation	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	C_2H_2
VDW	3.04	4.53	4.46	3.58	4.93
RSVDW	2.49	3.59	3.24	2.97	4.21
RK	0.92	1.14	0.94	1.37	2.36
RSRK	0.43	0.81	0.44	0.86	1.63

* Experimental values abstracted from Canjar and Manning (9).

pressures are

1. VDW ...... + 1962%
2. RSVDW ... + 222%
3. RK .... + 92%
4. RSRK ...... − 4.8%

From these results, and the data shown in Table 5, one has the impression that the RSRK equation follows the critical isotherm rather well at above-critical pressures. It also appears that the RSRK equation is the best of these four for the calculation of thermodynamic properties (gas phase) at temperatures less than the critical.

Calculated Fugacities

Table 6 summarizes the results of calculations of fugacity coefficients for the saturated vapors of methane, ethane, propane, isobutane and acetylene. Again, the results show the improved accuracy of predictions by substitution of (5) for the kinetic theory rigid-sphere expression (2) in the equation of state models. The fugacities were computed according to the following scheme:

1. Solve for a gas density such that the calculated pressure agrees with the experimental vapor pressure for a fixed temperature;
2. Solve for fugacity coefficient with the fixed temperature and the calculated density.

Although it is not the specific object of this study to propose a new or modified equation of state model for real fluids, it is interesting to note the generally more accurate prediction of saturated vapor fugacity by the RSRK equation. Such an improvement over the Redlich-Kwong equation could be useful in such correlations of vapor-liquid equilibrium as the Chao-Seader method (*10*), which uses the RK equation to predict vapor fugacity coefficients.

Yet, the point to be stressed is that the use of the more accurate rigid-sphere Equation (5) improves the ability of the real fluid equation of state model to predict thermodynamic properties for a wide variety of materials.

Discussion

The results presented above show one type of empirical application in which the rigid-sphere Equation (5) can be used in an approximate model of the real fluid equation of state.

The calculations of enthalpies, densities, isothermal pressures and fugacities (summarized in Tables 3, 4, 5, and 6) generally verify the hypothesis that the accurate rigid-sphere Equation (5) improves the model of the equation of state for real fluids. The calculations also show that the shortcomings of the original van der Waals' Equation (15) are not all attributable to the kinetic theory term used for the repulsion pressure P_R. The Redlich-Kwong modification of the cohesion term P_A appears to halve the average uncertainty in calculated enthalpies, using the kinetic theory term Equation (2) for repulsion pressure P_R. Yet, the combined effect of using the more accurate repulsion term (5) and the Redlich-Kwong cohesion term (18) is to cut the average uncertainty in the calculated enthalpies by a factor of approximately five, relative to the original van der Waals equation.

The study has used the van der Waals Equation (15) and the Redlich-Kwong Equation (17) as examples of equation of state models which can be improved with the substitution of (5) for the kinetic theory rigid-sphere term (2). Although these are both two-constant equations of state models, the resulting improvement should be considered general for any equation of state which presently uses the kinetic theory term (2) or its equivalent to describe repulsion effects in real fluids. At a time when so many researchers are publishing new and/or modified equations of state (of the Redlich-Kwong variety), it should prove worthwhile to use (5) for the repulsion model and then to focus attention on developing an improved cohesion term P_A.

MIXTURES

The generalized models of the equation of state, discussed above for pure fluids, are extended to calculate properties of mixtures. Again, attention is not to be focused upon the particular models of the equation of state used in the study. Emphasis is upon the overall improvement in the accuracy of the calculated thermodynamic properties when an accurate mixture rigid-sphere Equation (11) is used to describe the effects of intermolecular repulsions.

Coefficients for Mixture Equations

The majority of calculations of thermodynamic properties of mixtures from equations of state use the same algebraic form for multicomponent systems as for single-component systems. For mixtures, the equation of state coefficients are somehow averaged from the pure component coefficients. In practice, the averaging methods are usually chosen on the basis of accuracy in one of the predicted properties.

In the particular examples used in this paper, the van der Waals equation and the Redlich-Kwong equation, the mixing rules are usually as follows:

$$b_m = \sum_i x_i b_i \qquad (22)$$

$$a_m = [\sum_i x_i a_i^{1/2}]^2 \qquad (23)$$

This particular combining procedure for a and b is known as the linear-Berthelot rule, that is, a linear combination of the covolume b and a geometric average for the force parameter a.

Determining the validity of mixing rules has been the subject of much investigation of scientists and engineers who study mixture behavior. In order to see why this has been difficult in the simple case of the van der Waals equation, it is instructive to write the mixture van der Waals equation using the rigid-sphere mixture Equation (25) instead of the simple kinetic theory term.

$$P = RT_\rho\, Z_{rsm} - a\rho^2 \qquad (24)$$

and

$$Z_{rsm} = (1 + \alpha Y + \nu Y^2 - \gamma Y^3)/(1 - Y)^3 \qquad (25)$$

where

$$\alpha = 1.0 - \{ \sum_{i<j} x_i x_j (\sigma_i - \sigma_j)^2 (\sigma_i + \sigma_j)\} (3/<\sigma^3>)$$

$$\nu = 1.0 - \{ \sum_{i<j} x_i x_j (\sigma_i - \sigma_j)^2 (\sigma_i \sigma_j)\} (3<\sigma^2>/<\sigma^3>^2)$$

$$\gamma = <\sigma^2>^3/<\sigma^3>^2$$

$$Y = \pi N <\sigma^3>/6V$$

$$<\sigma^n> \equiv \sum_i x_i \sigma_i^n$$

TABLE 7. CALCULATED ENTHALPY DEPARTURES FOR MIXTURES
AVERAGE ABSOLUTE DEVIATION, B.t.u./lb. m

Equation	Mixture* A	B	C	D	E	F	G	H	I	J	K
VDW	2.74	2.63	5.77	10.78	9.51	9.20	3.33	12.18	17.90	24.3	28.2
RSVDW	1.94	2.09	4.77	8.85	6.62	6.67	1.77	9.07	14.29	19.27	22.3
RK	0.81	1.03	2.16	4.19	3.56	4.02	0.23	5.59	10.02	13.62	16.15
RSRK	0.62	0.72	1.23	2.65	1.76	2.41	1.14	3.46	7.59	10.1	11.80

* *A* = 94.8% methane, 5.2% propane (Molar basis).
B = 88.3% methane, 11.7% propane.
C = 72.0% methane, 28.0% propane.
D = 49.4% methane, 50.6% propane.
E = 38.5% pentane, 61.5% cyclohexane.
F = 61.2% pentane, 38.8% cyclohexane.
G = 56.6% methane, 43.4% nitrogen.
H = 19.7% pentane, 80.3% cyclohexane.
I = 80.9% pentane, 19.1% octane
J = 59.7% pentane, 40.3% octane.
K = 39.5% pentane, 60.8% octane.

If the linear mixing rule were valid for the covolume b, then the coefficients α, ν, and γ would all have to be unity.

Thus, instead of the repulsion contribution to the pressure being calculated by the simple kinetic theory term (with an averaged value of the covolume b), the repulsion effect is calculated using several different types of averages of the pure component covolumes. Recall, for a single component, the molar covolume is

$$b = (2\pi N/3)\sigma^3 \qquad (26)$$

Also, for the generalized equations of state, b is usually related to the critical point properties, for example,

$$b = \beta\, RT_c/P_c, \qquad (27)$$

where β = constant for a given equation of state. So

$$\sigma_i = (\beta\, RT_{ci}/P_{ci})(3/2\pi N), \qquad (28)$$

and

$$\sigma_i^2 = (\sigma_i^3)^{2/3} = b_i^{2/3}\ (3/2\pi N)^{2/3} \qquad (29)$$

$$\sigma_i = (\sigma_i^3)^{1/3} = b_i^{1/3}\ (3/2\pi N)^{1/3} \qquad (30)$$

Using the length parameters σ_i obtained from the covolumes, the effect of the mixture rigid-sphere Equation (25) as a model of repulsion phenomena in real fluid mixtures is seen in the following study.

Enthalpy Departures of Mixtures

For the simple two-constant models of the equation of state used in this study, the algebraic form of the expression for enthalpy departures remains the same as for the pure fluids. The difference is that the rigid-sphere compressibility factor Z_{rs} is calculated from the mixture Equation (25) rather than from (5). The energy constant a is also replaced by the averaged value of the coefficient, that is, a_m from (23).

Using the mixture equation, densities were calculated for given temperature, pressure, and composition information. The densities, temperatures, and compositions were then used to calculate mixture enthalpy departures. The summarized results of the calculations for twelve binaries are presented in Table 7.

Discussion

The results shown in Table 7 verify, for mixtures, that the rigid-sphere Equation (25) is a more effective model of repulsion and collision phenomena in real fluids than the rigid sphere expressions of the van der Waals and Redlich-Kwong equations. The general effect is easily seen in the overall deviations between predicted and observed data. The overall results are

1. VDW .... 14.25 B.t.u./lbM
2. RSVDW .... 10.05 B.t.u./lbM
3. RK .... 6.50 B.t.u./lbM
4. RSRK .... 4.47 B.t.u./lbM

The use of the rigid-sphere equation roughly decreases the average deviation by a factor of one-third. Since the number of coefficients remains the same as in the original equations, the more accurate predictions are attributable to a better algebraic model of intermolecular repulsion effects.

CONCLUSIONS

The effectiveness of (5) as a model for the repulsion behavior of real fluids has been shown by several examples.

Equation (5) was used to replace the kinetic theory form of the rigid-sphere equation in the van der Waals equation and in the Redlich-Kwong equation. The accuracy of predicted enthalpies, densities, pressures, and saturation fugacities was improved, verifying that the rigid-sphere equation developed in this research can be used in approximate theories of real fluids as a more accurate model of repulsion behavior.

The improvement of the prediction of mixture enthalpy departures amplifies the conclusion that the accurate rigid-sphere equation of state, (5) is an effective model for the calculation of repulsion behavior in real fluids.

NOTATION

A = Helmholtz free energy
A^0 = Helmholtz free energy of an ideal gas
G = Gibbs free energy
G^0 = Gibbs free energy of an ideal gas at T, P of system
H = enthalpy
H^0 = enthalpy of an ideal gas at T, P of system
N = number of molecules in the system (Avogadro's number for a molar system)
P = total pressure
P_c = critical pressure
P_{rs} = rigid-sphere pressure
P_R = repulsion pressure
R = molar gas constant
S = entropy
S^0 = ideal gas entropy at T, P of system
T = absolute temperature
T_c = critical temperature, absolute
U = energy of the system
V = total volume of the system
Y = reduced density for rigid-sphere mixtures
Z = compressibility factor, PV/NkT
Z_c = critical compressibility factor
a, b = coefficients of two-constant equations of state
b = system covolume, $(2\pi N\sigma^3/3)$

d = density, $1/V$
d^* = reduced rigid-sphere mixture density, $6y/\pi$
f = fugacity
k = Boltzmann constant
n_i = reduced density of i-molecules, $x_i(\pi N/6V)$
x_i = mole fraction of i-molecules in system
y = reduced density in rigid-sphere equations

Greek Letters

β = general coefficient
ρ = density, $1/V$
Σ = summation operator
σ = rigid-sphere diameter
σ_i = sphere diameter of i-molecules
σ_{ij} = $1/2(\sigma_i + \sigma_j)$
ϕ = pressure due to cohesion and soft-repulsion $P - P_{rs}$

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The Effect of Angular Light Intensity Distribution on the Performance of Tubular Flow Photoreactors

The angular light intensity distribution (ALID) at the surface of several elliptical reflector-photoreactors was determined experimentally using the optically dense potassium ferrioxalate actinometer. The distributions were well correlated by the model

$$I_w(\theta) = \overline{I_w}[1 + \beta\cos\theta]$$

The correlating parameter β was a function of the ratio of the light source and photoreactor tube diameters.

The theoretical effect of ALID on reactor performance was determined for a reaction which proceeded via direct absorption by the reactant. The ALID effect on performance was most pronounced under conditions of high optical densities and low radial mixing rates of reactant.

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SCOPE

The elliptical reflector-photoreactor has been used extensively in the investigation of photoreaction kinetics. The elliptical photoreactor consists of a tubular light source and a quartz reactor tube located at the foci of a reflector cavity whose cross section is elliptical. This construction was suggested by the fact that light rays originating from a light source located at one focus are reflected through a sink centered along the other focus. The light intensity distribution within the reactor is easily calculated if the light is assumed to enter normal to the reactor surface and is assumed to be uniformly intense about the circumference of the reactor.

Since the source must be of finite size some investigators have questioned this idealized model of light distribution and have proposed more realistic models. However, many such models retain the assumption that the incident light intensity is uniform with respect to the angular direction at the reactor surface.

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