

Equations A4 and A5 have a feasible solution

$$Da_i > 0 \quad i = 1, 2, \dots, N \quad (A8)$$

if and only if the hyperplane defined by these equations intersects at least one of the planes bounding the positive region. Thus, at least one set of equations

$$a_i Da_i + a_j Da_j = 1 \quad (A9)$$

$$b_i Da_i + b_j Da_j = 1 \quad i \neq j = 1, 2, \dots, N \quad (A10)$$

has to be satisfied. These equations have a feasible solution only if reactions i and j can lead to multiplicity for some Da_i and Da_j . Thus, unless at least one of the $N(N + 1)/2$ criteria (Eqs. 60 and 61) is satisfied multiplicity cannot occur.

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Manuscript received February 19, 1982; revision received July 6, and accepted August 26, 1982.

Chain-of-Rotators Equation of State

An equation of state is obtained to describe the fluid state from the supercritical gas to subcritical vapor and liquid for small and large molecules of organic and inorganic substances. The perturbation theory of the fluid state is extended to include rotational contribution of molecular motion in addition to translational and the attractive force contributions. Three equation constants describe a substance and values are presented for 22 substances. Application is made to mixtures with emphasis on their phase equilibria.

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SCOPE

The design of processes involving fluid mixtures, especially separation processes, requires quantitative information about the thermodynamic properties of fluids and their mixtures. The diversity of fluid mixtures encountered in such processes precludes a compilers approach to estimating fluid properties. Likewise extensive experimental data are seldom available except for a limited number of mixtures and even then restricted in range of composition, temperature and pressure. There continues to be a need to interpolate and extend fragmentary data to predict and design processes. Equations of state are useful to satisfy this need.

The objective of this work is to develop an equation of state generally useful for molecular fluids over a wide range of fluid

states including the supercritical gas and the subcritical vapor and liquid of pure fluids and fluid mixtures. Perturbation theory of fluid state is extended to chain molecules with the introduction of a new partition function to describe the rotational contribution of molecules to configurational properties. An equation of state, called the chain-of-rotators (COR) equation, is obtained from the partition function. Only three substance-specific parameters are required to be known for a fluid to be described by the new equation. Values of the parameters have been determined and are reported here for 22 substances.

The new equation is applied to mixtures with the use of Van der Waals one fluid mixing rules.

CONCLUSIONS AND SIGNIFICANCE

The new equation of state gives a generally good description of fluid states for molecular fluids. Good results are obtained in pVT , vapor pressure, and enthalpy calculations.

The new equation describes fluid-phase equilibrium for diverse mixtures including azeotrope-forming systems. Symmetric mixtures of comparable components as well as asymmetric

mixtures of a light gas and a heavy solvent are equally well represented. Correlation of binary interaction constants has been developed for some common mixture systems.

A major advantage of the new equation is that it is readily applied to new substances since only three parameters need be known for each substance. The new equation should be par-

ticularly useful for fluids of large molecules for which experimental thermodynamic data are scarce. The new equation appears suitable for phase equilibrium and thermodynamic property calculations in engineering design of chemical processes.

Equations of state are widely used for the calculation of fluid properties in chemical process engineering. The usefulness of equations of state has prompted a continual development of new equations.

Empirical equations have been devised for the accurate fitting of observed data. The equations greatly facilitate the differentiation and integration of the data to obtain derived thermodynamic properties. Accuracy of fitting is achieved with the use of a large number of empirical terms and a correspondingly large number of equation parameters for each substance. The Benedict-Webb-Rubin (BWR) equation (1940) contains eight parameters. Starling's (1973) extended BWR equation contains 11. Goodwin's equation (1974) for methane is widely used as the reference fluid equation in shape factor corresponding state calculations in spite of its inconvenience for being nonanalytical. Jacobsen's equation (1972) containing 33 constants originally developed for nitrogen has been applied to several light substances by the IUPAC Thermodynamic Tables Project.

Cubic equations have received much attention ever since van der Waals (1873) succeeded in describing qualitatively the continuity of the gas and liquid states. Redlich and Kwong (1949) showed that a cubic equation can be of quantitative interest. Soave's (1972) and Peng and Robinson's (1976) equations are useful in some quantitative applications. The cubic equations offer the special advantage of an algebraic, rather than numerical, solution for the volume at a given temperature and pressure. The cubic equations can be very useful but are so far oversimplifications.

PERTURBATION THEORY

The structure of a fluid is primarily determined by the short-range repulsive forces. The long-range attractive forces play a lesser part in the structure and can be considered as a perturbation. Perturbation theory has contributed much to the understanding of dense fluids (Henderson, 1979) in recent years. The partition function of a fluid is correspondingly decomposed into one part pertaining to the hard-core repulsion and another pertaining to the perturbative attraction.

$$Q_{\text{conf}} = Q_{\text{rep}}Q_{\text{attr}} \quad (1)$$

Equation 1 embodies the concept of van der Waals and directly leads to the van der Waals' equation of state when the repulsive and attractive forces are appropriately simplified.

For simple fluids, the reference hard cores are hard spheres, and the reference fluid partition function describes translational motion

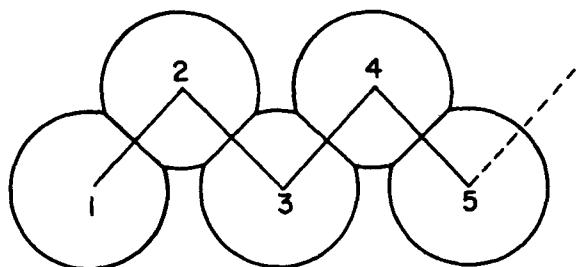


Figure 1. Chain molecule.

of the hard spheres. Additional modes of rotation and vibration contribute to the partition function of complex molecules. For a chain molecule such as shown in Figure 1, Prigogine (1957) suggested treating the first segment like a free molecule. The second segment rotates on a spherical surface about the first segment. Segment 3 moves with one new degree of freedom (on a circle) if the angle 1 2 3 is fixed by the valency forces. On the other hand, if the angle 1 2 3 is free, segment 3 rotates much like segment 2. This procedure is continued for all segments of the chain. The rotational degrees of all segments and the translational motion of the entire molecule may be combined to reexpress Q_{rep} of Eq. 1 and obtain

$$Q_{\text{conf}} = Q_t q_r^N Q_{\text{attr}} \quad (2)$$

where Q_t is the translational partition function; q_r , the partition function of an elementary rotator; N , the number of molecules; and c , the rotational degrees of freedom of the molecular chain. The more flexible the chain, the greater the value of c ; the less flexible, the smaller the value of c . For nonchain molecules the precise assignment of rotational degrees to the individual segment is not obvious; the expression q_r^c gives an overall expression of the total rotational modes of the entire molecule.

Because a configurational rotational partition function was not known at the time, Prigogine replaced q_r with an equivalent translational partition function. Hijmans (1961), Flory (1970), and Patterson and Delmas (1970) also developed equations of state for large molecules on this basis. The equations apply to liquids but give incorrect results at low densities as they do not approach the ideal gas law. Beret and Prausnitz (1975) extended the equivalent translational approach by constructing a partition function that is the simplest function to satisfy the boundary conditions including the ideal gas law at infinite volume. There is no other basis for the proposed partition function.

PARTITION FUNCTIONS

To obtain an equation of state from Eq. 2, we express the partition functions as functions of N , V and T . For the translational, we use the partition functions obtained by Nitta et al. (1977) from Carnahan and Starling's hard-sphere equation of state,

$$Q_t = \frac{V^N}{N!} \exp \left[- \frac{N \left(4 \frac{\bar{v}}{\tau} - 3 \right)}{\left(\frac{\bar{v}}{\tau} - 1 \right)^2} \right] \quad (3)$$

where \bar{v} is the reduced volume defined as V/V_0 , V_0 is the closest packed volume and $\tau = \pi\sqrt{2}/6 = 0.7405$.

For the rotational partition function, we will first obtain an expression for an elementary rotator by combining Eq. 2 with the equation of state of hard dumbbell molecules obtained by Boublik and Nezbeda (1977) from computer simulated data

$$p_{db} = \frac{NkT}{V} \left[\left(\frac{\bar{v}}{\tau} \right)^3 + (3\alpha - 2) \left(\frac{\bar{v}}{\tau} \right)^2 + (3\alpha^2 - 3\alpha + 1) \left(\frac{\bar{v}}{\tau} \right) - \alpha^2 \right] / \left(\frac{\bar{v}}{\tau} - 1 \right)^3 \quad (4)$$

where α is a dumbbell constant given in terms of L the ratio of the

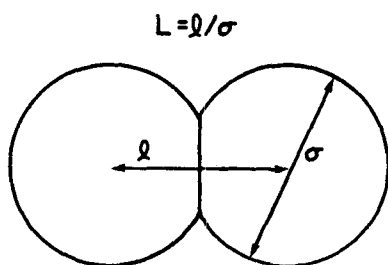


Figure 2. Dumbbell molecule.

spheres' center-to-center distance l to the diameter of the spheres σ shown in Figure 2.

$$L = l/\sigma \quad (5)$$

$$\alpha = \frac{(1+L)(2+L)}{2+3L-L^3} \quad \text{for } L \leq 1 \quad (6)$$

Equation 4 has been used by Kohler et al. (1979) and Fischer (1980) as the reference repulsive pressure in their perturbation theory for diatomic molecules. Results indicate that Eq. 4 accurately describes the repulsive pressure of these diatomic fluids.

Upon integrating Eq. 4 according to

$$\left(\frac{\partial \ln Q_{db}}{\partial V} \right)_{T,N} = \frac{p_{db}}{kT} \quad (7)$$

and making use of the boundary condition that as $V \rightarrow \infty$, $Q_{db} = V^N/N!$ we obtain the partition function of N hard dumbbells

$$Q_{db} = \frac{V^N}{N!} \left\{ \left(\frac{\tilde{v}}{\tau} \right)^{\alpha^2-1} \exp \left[- \frac{(\alpha^2 + 3\alpha) \frac{\tilde{v}}{\tau} - 3\alpha}{\left(\frac{\tilde{v}}{\tau} - 1 \right)^2} \right] \right\}^N \quad (8)$$

A hard dumbbell molecule is a chain molecule of two segments, having three translational degrees of motion, two rotational degrees, and no attractive forces. For an assembly of hard dumbbells, Eq. 2 simplifies to

$$Q_{db} = Q_1 q_r^{2N} \quad (9)$$

Upon combining Eqs. 3, 8, and 9 we have

$$q_r = \left(\frac{\tilde{v}/\tau}{\tilde{v}/\tau - 1} \right)^{(\alpha^2-1)/2} \exp \left[- \frac{(\alpha^2 + 3\alpha - 4) \frac{\tilde{v}}{\tau} - 3(\alpha - 1)}{2 \left(\frac{\tilde{v}}{\tau} - 1 \right)^2} \right] \quad (10)$$

In the limit of $V \rightarrow \infty$, Eq. 10 gives $q_r \rightarrow 1$ and the rotational modes make no contribution to configurational properties in the ideal gas state. This is shown in Figure 3 in terms of the compressibility factor $Z_r = p_r V / (NkT)$ of a pure rotator derived from Eq. 10. At the limit of zero density Z_r approaches zero. Z_r remains minor for dilute gases and becomes significant only at high densities. For comparison we also show Z_t of Carnahan and Starling's equation of state. Z_t is always significant even at the limit of zero density where it approaches 1.

The perturbation attraction term Q_{attr} was expressed by Alder et al. (1972) in terms of a power series for a square well fluid.

$$Q_{attr} = \exp \left[- \frac{Nu}{kT} \sum_{n,m} \frac{A_{nm}}{\tilde{T}^{n-1} \tilde{v}^m} \right] \quad (11)$$

where u is the characteristic energy, $T^* = u/k$, and $\tilde{T} = T/T^*$.

Donohue and Prausnitz (1978) fitted a similar double sum expression to the experimental data on methane. Chen and Kreglewski (1977) fitted the expression to the residual energy and volumetric data of argon. For nonspherical molecules, Chen and

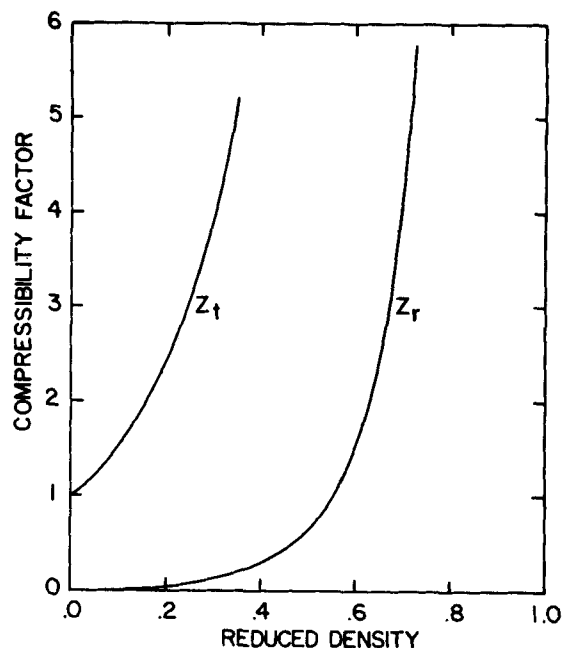


Figure 3. Compressibility factor of elementary rotators with $\alpha = 1.078$, $c = 1$, and compressibility factor of hard spheres.

Kreglewski found u/k to be temperature dependent. Our data reduction leads to a similar result which is best expressed by

$$u/k = T^* \left[1 + \frac{c}{2} (B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \quad (12)$$

For simple molecules, $c = 0$ and we recover $u/k = T^*$. In the case of $B_1 = 0$ and $B_2 = 0$, Eq. 12 reduces to

$$u/k = T^* \left(1 + \frac{c}{2} B_0 \right) \quad (13)$$

which is similar to Beret and Prausnitz' definition of T^* . With $B_2 = 0$, Eq. 12 simplifies to the form of Chen and Kreglewski. Values of B_0 , B_1 , and B_2 that we have determined from data reduction are presented in Table 1.

The complete configurational partition function is obtained by combining Eqs. 3, 10, 11 and 12 with Eq. 2,

$$Q_{conf} = \frac{V^N}{N!} \exp \left[- \frac{N \left(4 \frac{\tilde{v}}{\tau} - 3 \right)}{\left(\frac{\tilde{v}}{\tau} - 1 \right)^2} \right] \times \left\{ \left(\frac{\tilde{v}}{\tau} \right)^{(\alpha^2-1)} \frac{\tilde{v}}{\tau} - 1 \right\} \times \exp \left[- \frac{(\alpha^2 + 3\alpha - 4) \frac{\tilde{v}}{\tau} - 3(\alpha - 1)}{\left(\frac{\tilde{v}}{\tau} - 1 \right)^2} \right] \right\}^{Nc/2} \exp \left\{ -N \left[1 + \frac{c}{2} (B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_{n,m} \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} \right\} \quad (14)$$

Values of the coefficients A_{nm} that we have determined from data reduction are presented in Table 1.

WORKING EQUATIONS

The chain-of-rotators (COR) equation of state is derived from

TABLE 1. UNIVERSAL CONSTANTS B_0 , B_1 , B_2 AND ANM
 $B_0 = 0.20095$, $B_1 = 0.019$, $B_2 = -0.0632$

A_{nm} n	1	2	3	4	5	6
1	-9.04214	-125.11	525.415	-859.803	634.635	-167.336
2	-1.12517	548.709	-2,566.20	4,471.80	-3,402.75	939.226
3	-0.809958	-838.503	4,398.77	-8,598.81	7,409.90	-2,365.34
4	-0.672378	438.783	-2,482.01	5,289.80	-5,017.09	1,784.58

the partition function of Eq. 14 by following standard procedures of statistical thermodynamics (Reed and Gubbins, 1973).

$$\frac{pV}{nRT} = 1 + \frac{4\left(\frac{\bar{v}}{\tau}\right)^2 - 2\left(\frac{\bar{v}}{\tau}\right)}{\left(\frac{\bar{v}}{\tau} - 1\right)^3} + \frac{c}{2}(\alpha - 1) \frac{3\left(\frac{\bar{v}}{\tau}\right)^2 + 3\alpha\left(\frac{\bar{v}}{\tau}\right) - (\alpha + 1)}{\left(\frac{\bar{v}}{\tau} - 1\right)^3} + \left[1 + \frac{c}{2}(B_0 + B_1/\tilde{T} + B_2\tilde{T})\right] \sum_{n,m} \frac{mA_{nm}}{\tilde{T}^n \bar{v}^m} \quad (15)$$

From Eq. 15 we obtain the second virial coefficient

$$\frac{B}{V_0} = \tau \left[4 + \frac{3c}{2}(\alpha - 1) \right] + \left[1 + \frac{c}{2}(B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_n \frac{A_{n1}}{\tilde{T}^n} \quad (16)$$

Standard thermodynamic derivation (Chao and Greenkorn, 1975) from Eq. 15 gives the internal energy

$$\frac{U}{nRT} = \left[1 + \frac{c}{2}(B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_{n,m} \frac{nA_{nm}}{\tilde{T}^n \bar{v}^m} + \frac{c}{2}(B_1/\tilde{T} - B_2\tilde{T}) \sum_{n,m} \frac{A_{nm}}{\tilde{T}^n \bar{v}^m} + \frac{U^\circ}{nRT} \quad (17)$$

and the fugacity ratio,

$$\ln(f/p) = -\ln\left(\frac{pV}{nRT}\right) + \frac{4\frac{\bar{v}}{\tau} - 3}{\left(\frac{\bar{v}}{\tau} - 1\right)^2} - \frac{c}{2}(\alpha - 1) \left[(\alpha + 1) \ln \frac{\frac{\bar{v}}{\tau}}{\left(\frac{\bar{v}}{\tau} - 1\right)} - \frac{(\alpha + 4)\frac{\bar{v}}{\tau} - 3}{\left(\frac{\bar{v}}{\tau} - 1\right)^2} \right] + \left[1 + \frac{c}{2}(B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_{n,m} \frac{A_{nm}}{\tilde{T}^n \bar{v}^m} + \frac{pV}{nRT} - 1 \quad (18)$$

The equation for entropy is obtained by combining Eqs. 17 and 18,

$$S = \frac{U - U^\circ}{T} - nR \left(\ln \frac{f}{p} + 1 - \frac{pV}{nRT} \right) + S^\circ \quad (19)$$

DATA REDUCTION

The coefficients A_{nm} were determined by fitting the working equations to the pVT , $U - U^\circ$, and vapor pressure data of methane for which the rotational degree is considered absent, that is $c = 0$. The fitting was based on parameter values of methane: $V_0 = 21.192$ cm³/gmol from the closest packed volume at critical temperature reported by Chen and Kreglewski, and $T^* = 151.71$ K. Four of the A_{nm} constants A_{11} , A_{21} , A_{31} , and A_{41} were fitted to the second virial coefficient of methane in Dymond and Smith (1969). The re-

maining constants were then determined by fitting the pVT , $U - U^\circ$, and vapor pressure data.

The constants B_0 , B_1 , B_2 and α that apply to rotational contributions were determined by referring to ethane data. Molecules of ethane possess two degrees of rotation and hence $c = 2$. The bond length l of ethane is 0.1536 nm and the diameter σ of methyl group is 0.3679 nm from the value of V_0 of methane. From Eq. 5, $L = 0.4175$, and from Eq. 6, $\alpha = 1.078$. With c and α known, we determine V_0 and T^* of ethane as well as the universal constants B_0 , B_1 , and B_2 by fitting vapor pressure data of ethane.

Because of their high triple points, all the fluid state data on methane and ethane are confined to relatively high values of \tilde{T} . To reach the region of low \tilde{T} , we made use of propane data. Initial fitting was made of the high \tilde{T} vapor pressure data to determine V_0 , T^* and c for propane. Finally, adjustment was made of the universal A and B constants to fit the pVT , $U - U^\circ$ and vapor pressure data of propane, as well as those of methane and ethane. No changes were made of the constants A_{11} through A_{41} as these were separately related to the second virial coefficient of methane.

The rotator parameter $\alpha = 1.078$ was obtained for the single bond between two carbon atoms. In this work, this value of α is used for all rotators of all molecules. The strongest dependence on α is found in the factor $(\alpha - 1)$ in the rotational contribution term in Eq. 15 and is in the form of a product with c . By fixing α we in essence employ equivalent rotators, and have evaluated equivalent values of c . The use of equivalent rotators simplifies calculations. Future improvement may call for different α values for different rotators.

More details of data reduction may be found in Chien (1981).

PURE FLUIDS

Except for methane, ethane, and propane, COR equation parameters have been obtained by fitting the equation to vapor pressure and saturated liquid density data of pure fluids. Table 2 presents the equation parameters for 22 substances.

The COR equation calculated vapor pressures are illustrated in Figure 4 with the paraffins from methane to n-hexadecane. The calculated saturated liquid molal volumes are shown in Figure 5 for N₂, CO, CO₂, and Ar. Figure 6 shows the calculated isotherms for propane over the very wide temperature range 90–600 K, and Figure 7 shows the enthalpy deviation at the same temperatures. In all the figures it is almost impossible to see the deviations except for the low-temperature enthalpies.

Tables must be employed to present meaningful comparison between the COR equation and experimental data. In Table 3 we present the summary comparison of saturated fluid data for 12 substances. A detailed comparison is presented in Table 4 for benzene. Comparisons with experimental pVT data are summarized in Table 5 for six substances. A detailed comparison is presented in Table 6 for ethylene. Additional extensive comparisons have been made by Chien (1981).

The COR equation calculated vapor pressures are generally within 1% of experimental data. Deviation tends to be higher at low temperatures for vapor pressures below 0.01 MPa. The calculated liquid densities are generally within 0.5%.

The COR equation and the perturbed hard chain (PHC) equation of Donohue and Prausnitz (1977) are both based on perturbation theory. Both equations use three parameters for each sub-

TABLE 2. EQUATION OF STATE PARAMETERS FOR SOME SUBSTANCES

$$\alpha = 1.078$$

Substance	T^*, K	c	$V_o, \text{cm}^3/\text{mol}$
Methane	151.71	0	21.192
Ethane	225.44	2.0	30.52
Propane	263.57	3.2	41.51
n-Butane	293.25	4.4	52.24
n-Pentane	315.61	5.6	63.10
n-Hexane	333.87	6.8	73.96
n-Octane	356.55	9.6	95.68
n-Decane	372.70	12.4	117.40
n-Hexadecane	409.17	19.36	184.38
Isobutane	286.27	3.8	52.70
Isopentane	311.11	5.2	63.00
Neopentane	297.54	4.50	63.85
Cyclohexane	375.98	4.92	63.00
Methylcyclohexane	381.49	5.70	74.96
Cyclopentane	351.01	4.50	53.25
Ethylene	211.00	1.7	27.30
Benzene	384.44	4.8	52.25
Toluene	395.20	6.0	63.4
N ₂	97.75	0.64	19.02
CO	106.09	0.20	19.00
CO ₂	205.52	5.2	19.00
H ₂ S	278.82	1.7	20.50

TABLE 3. SUMMARY COMPARISON OF COR AND PHC EQUATIONS WITH SATURATED PURE FLUID DATA

(A) Vapor Pressure

Substance	No. of Data Points	Temp. Range, K	Pres. Range, MPa	COR Av %Dev	PHC Av %Dev	Data Source
Methane	21	91/190	0.012/4.5	0.79	0.56	Prydz and Goodwin (1972)
Ethane	13	100/301	10 ⁻⁵ /4.5	1.98	1.12	Ziegler/Pal in Goodwin et al. (1976).
Propane	22	116/361	10 ⁻⁶ /3.6	1.57	2.42	Sage and Lacey (1950); Tickner/Kemp/Douslin
n-Butane	23	135/419	6 × 10 ⁻⁷ /3.4	0.83	1.61	Sage and Lacey (1950); Thermaloops/Hirata in Goodwin (1979)
Isobutane	8	315/405	0.55/3.4	0.59	3.10	Sage and Lacey (1950)
n-Pentane	10	311/461	0.11/2.9	0.52	1.25	Sage and Lacey (1950)
Benzene	42	273/555	3 × 10 ⁻³ /4.5	1.34	2.02	Young/Fiock/Schmidt/Smith and Menzies/Schamhardt in Timmermans (1950)
Toluene	36	287/593	2 × 10 ⁻³ /4.2	1.26	2.22	Schmidt/Willingham et al. Zmaczynski/Krase and Goodman in Timmermans (1950)
n-Octane	24	273/553	4 × 10 ⁻⁴ /2.0	0.56	2.01	Young/Willingham et al. in Timmermans (1950)
Ethylene	14	136/273	8 × 10 ⁻³ /4.1	0.81	1.15	Crommelin et al., Egan and Kemp in Timmermans (1950)
H ₂ S	11	284/369	1.4/8.3	0.57	0.89	Sage and Lacey (1955)
CO ₂	40	271/302	0.52/7.1	0.45	0.59	Sage and Lacey (1955); Kuenen and Robson/Meyers and Duson/ Michels in Timmermans (1950)

(B) Saturated Liquid Volume

Substance	No. of Data Points	Temp. Range, K	COR Av %Dev	PHC Av %Dev	Data Source
Methane	11	105/160	0.04	0.68	Haynes and Hiza (1977)
Ethane	21	100/301	0.53	2.18	Haynes/Sliwinski in Goodwin et al. (1976).
Propane	21	87/361	0.21	1.29	Sage and Lacey (1950) Orrit/Douslin in Goodwin (1977)
n-Butane	25	138/419	0.45	1.24	Sage and Lacey (1950); Kay/Orrit/Sliwinski in Goodwin (1979)
Isobutane	8	315/405	1.13	2.70	Sage and Lacey (1950)
n-Pentane	10	311/461	0.34	1.04	Sage and Lacey (1950)
Benzene	15	273/553	0.14	1.26	Young in Timmermans (1950)
Toluene	4	250/400	0.27	0.47	Massart in Timmermans (1950)
n-Octane	15	273/553	0.69	2.40	Young in Timmermans (1950)
Ethylene	7	128/279	1.05	5.06	Mathias in Timmermans (1950)
H ₂ S	11	284/369	0.71	3.19	Sage and Lacey (1955)
CO ₂	26	280/301	1.14	2.77	Lowry and Erickson/Michels in Timmermans (1950)

(C) Saturated Vapor Volume

Substance	No. of Data Points	Temp. Range, K	COR Av %Dev	PHC Av %Dev	Data Source
Ethane	10	100/280	3.19	2.82	Virial in Goodwin et al. (1976)
Propane	16	160/361	3.06	5.20	Virial/Sliwinski in Goodwin (1977)
n-Butane	18	200/419	1.92	3.69	Sage and Lacey (1950) Virial/Sliwinski in Goodwin (1979)
n-Pentane	10	311/461	3.15	5.93	Sage and Lacey (1950)
Benzene	11	353/553	2.01	5.54	Young in Timmermans (1950)
Ethylene	4	210/279	2.35	13.05	Mathias et al. in Timmermans (1950)

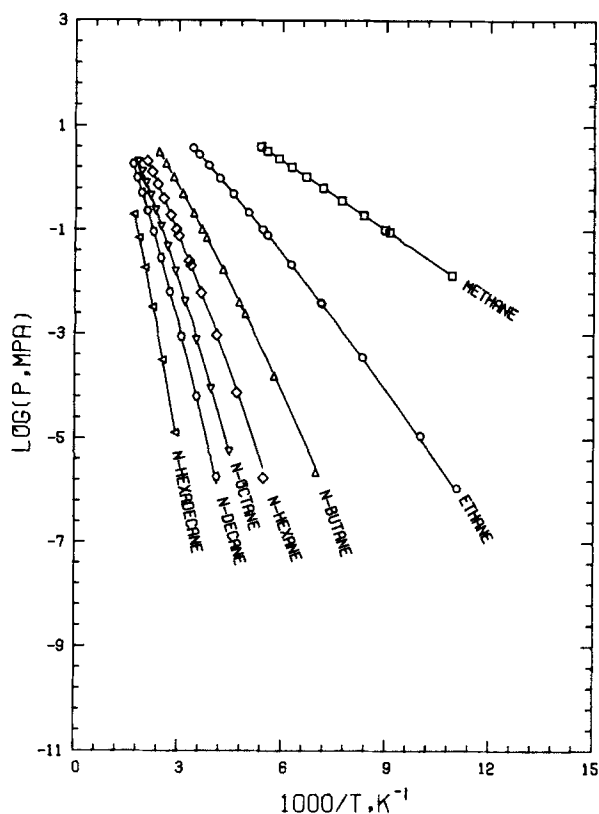


Figure 4. Vapor pressure of normal paraffins.

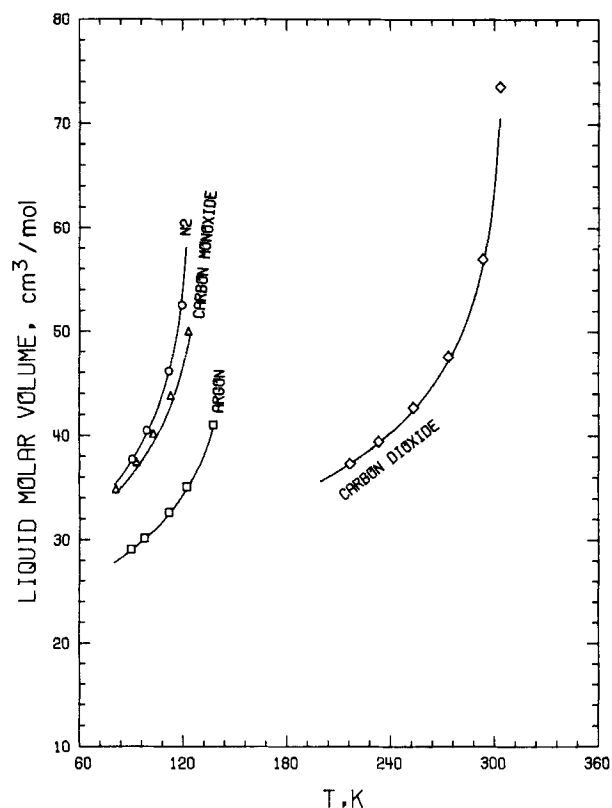


Figure 5. Saturated liquid molar volume of some inorganic substances.

stance. Since the PHC equation is a major recent development, it is included in Tables 3 through 6. Equation parameters given by Donohue and Prausnitz are used in the PHC calculations. For simple fluids and nearly simple fluids, both equations give comparable vapor pressures while the COR equation gives better

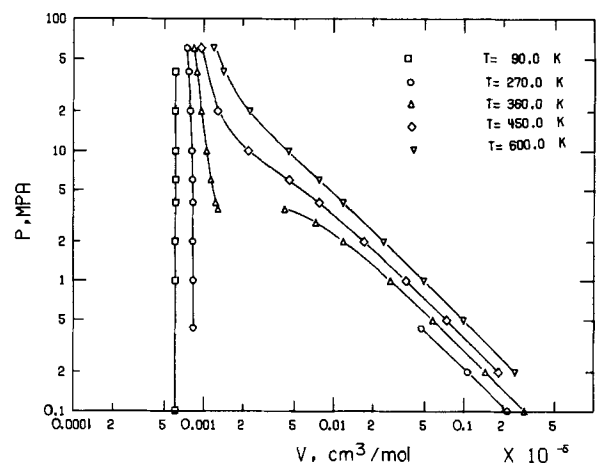


Figure 6. pVT of propane.

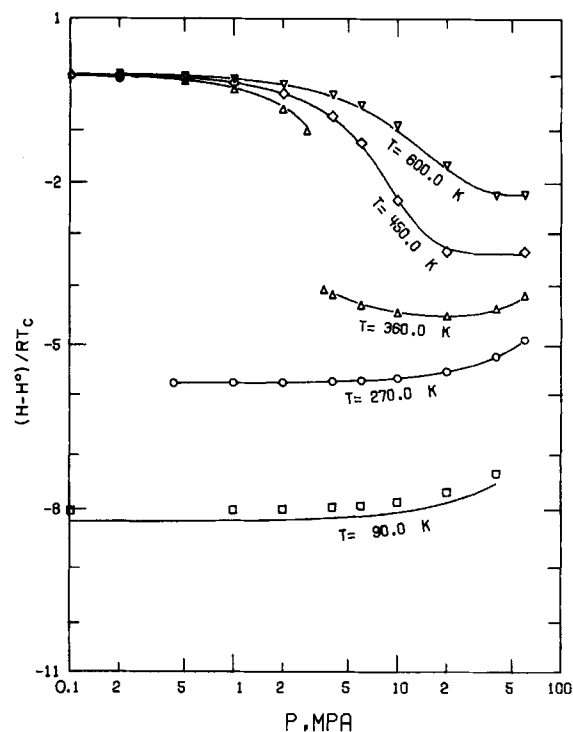


Figure 7. Enthalpy departure of propane.

densities. Increasing structural complexity of the molecules give more favorable results to the COR equation in all properties. Improvement in accuracy by a factor of two is generally indicated for molecules beyond propane.

Cubic equations are in wide use for VLE calculations, but are at best fair representations of pVT behavior of fluids. Martin (1979) gave an extensive comparison of six cubic equations with pVT data on ethylene. The same data are used in Table 6 with the cubic equation results omitted. Interested readers are referred to Martin's article. These experimental conditions do not reach low reduced temperature liquids and, therefore, do not provide a severe test. For these relatively mild conditions, the COR equation gives equally good or better results.

MIXING RULES AND FUGACITY EQUATION

The COR equation of state applies to mixtures with the introduction of mixing rules for the equation constants. Since the COR

TABLE 4. DETAILED COMPARISON OF COR AND PHC EQS. WITH SATURATED FLUID DATA OF BENZENE

ID References

1 = Young (1910) in Timmermans (1950)

2 = Fiock et al. (1931) in Timmermans

3 = Schmidt (1934) in Timmermans

4 = Smith and Menzies (1910) in Timmermans

5 = Schamhardt (1908) in Timmermans

Schmiedt (1999) in Rinnhermans						
ID	T,K	P,MPa	(A) Vapor Pressure	PCNT	PHC,CALD	PCNT
			COR,CALD			
1	273.150	3.5400E-03	3.6800E-03	3.86	3.7800E-03	6.81
1	293.150	9.8800E-03	1.0260E-02	3.80	1.0310E-02	4.29
1	313.150	2.4020E-02	2.4600E-02	2.38	2.4350E-02	1.34
1	333.150	5.1800E-02	5.2230E-02	0.83	5.1270E-02	-1.02
1	353.150	1.0066E-01	1.0055E-01	-0.11	9.8370E-02	-2.27
1	393.150	1.7799E-01	1.7870E-01	0.40	1.7490E-01	-1.73
1	373.150	2.9731E-01	2.9738E-01	0.02	2.9193E-01	-1.81
1	413.150	4.6930E-01	4.6862E-01	-0.14	4.6208E-01	-1.54
1	433.150	7.0660E-01	7.0560E-01	-0.14	6.9920E-01	-1.06
1	453.150	1.0155E+00	1.0226E+00	0.70	1.0177E+00	0.22
1	473.150	1.4199E+00	1.4352E+00	1.08	1.4328E+00	0.91
1	493.150	1.9360E+00	1.9603E+00	1.26	1.9597E+00	1.23
1	513.150	2.5801E+00	2.6177E+00	1.46	2.6144E+00	1.33
1	533.150	3.3769E+00	3.4315E+00	1.62	3.4138E+00	1.09
1	553.150	4.3706E+00	4.4375E+00	1.53	4.3765E+00	0.13
2	273.150	3.5400E-03	3.6800E-03	3.93	3.7800E-03	6.87
2	293.150	9.9500E-03	1.0260E-02	3.10	1.0310E-02	3.59
2	313.150	2.4150E-02	2.4600E-02	1.86	2.4350E-02	0.83
2	333.150	5.1810E-02	5.2230E-02	0.81	5.1270E-02	-1.04
2	353.150	1.0047E-01	1.0055E-01	0.07	9.8370E-02	-2.09
2	373.150	1.7924E-01	1.7870E-01	-0.30	1.7490E-01	-2.42
2	393.150	2.9840E-01	2.9738E-01	-0.34	2.9193E-01	-2.17
3	282.010	5.6800E-03	5.9100E-03	4.14	6.0100E-03	5.87
3	291.740	9.2900E-03	9.5900E-03	3.24	9.6500E-03	3.87
3	303.880	1.6270E-02	1.6680E-02	2.53	1.6610E-02	2.10
3	313.400	2.4400E-02	2.4850E-02	1.84	2.4590E-02	0.79
3	323.150	3.5770E-02	3.6330E-02	1.57	3.5790E-02	0.05
3	336.480	5.8260E-02	5.8610E-02	0.60	5.7490E-02	-1.33
3	349.370	8.9580E-02	8.9430E-02	-0.17	8.7520E-02	-2.30
3	354.450	1.0522E-01	1.0461E-01	-0.57	1.0234E-01	-2.73
4	336.310	5.8540E-02	5.8270E-02	-0.46	5.7150E-02	-2.37
4	344.240	7.5150E-02	7.5920E-02	1.02	7.4350E-02	-1.07
4	353.450	1.0205E-01	1.0148E-01	-0.57	9.9280E-02	-2.72
4	368.820	1.5959E-01	1.5873E-01	-0.54	1.5530E-01	-2.68
4	379.120	2.0012E-01	2.0936E-01	4.62	2.0505E-01	2.46
4	393.080	2.9798E-01	2.9688E-01	-0.37	2.9143E-01	-2.20
5	503.250	2.2438E+00	2.2744E+00	1.36	2.2733E+00	1.32
5	514.470	2.6651E+00	2.6662E+00	0.04	2.6626E+00	-0.10
5	524.530	3.0598E+00	3.0598E+00	0	3.0504E+00	-0.30
5	530.290	3.2677E+00	3.3044E+00	1.12	3.2899E+00	0.68
5	544.330	4.0074E+00	3.9672E+00	-1.00	3.9306E+00	-1.92
5	554.570	4.5447E+00	4.5179E+00	-0.59	4.4517E+00	-2.05
AVG DEV				1.34		2.02
(B) Saturated Liquid Volume						
ID	T,K	VL,L/mol	COR,CALD	PCNT	PHC,CALD	PCNT
1	273.150	8.6790E-02	8.6930E-02	0.16	8.7090E-02	0.34
1	293.150	8.8870E-02	8.8940E-02	0.08	8.9000E-02	0.15
1	313.150	9.1080E-02	9.1080E-02	-0	9.1170E-02	0.09
1	333.150	9.3470E-02	9.3370E-02	-0.11	9.3590E-02	0.12
1	353.150	9.5900E-02	9.5850E-02	-0.06	9.6270E-02	0.38
1	373.150	9.8540E-02	9.8550E-02	0.01	9.9230E-02	0.70
1	393.150	1.0155E-01	1.0153E-01	-0.02	1.0252E-01	0.95
1	413.150	1.0499E-01	1.0486E-01	-0.12	1.0619E-01	1.14
1	433.150	1.0872E-01	1.0866E-01	-0.05	1.1033E-01	1.49
1	453.150	1.1311E-01	1.1309E-01	-0.02	1.1507E-01	1.74
1	473.150	1.1826E-01	1.1839E-01	0.11	1.2061E-01	1.98
1	493.150	1.2488E-01	1.2503E-01	0.12	1.2724E-01	1.89
1	513.150	1.3350E-01	1.3389E-01	0.29	1.3549E-01	1.49
1	533.150	1.4661E-01	1.4720E-01	0.40	1.4635E-01	-0.18
1	553.150	1.7305E-01	1.7399E-01	0.54	1.6208E-01	-6.34
AVG DEV				0.14		1.26

TABLE 4. (continued)

ID	T,K	VG,L/mol	(C) Saturated Vapor Volume		PCNT	PHC,CALD	PCNT
			COR,CALD				
1	353.150	2.8592E+01	2.8413E+01		-0.63	2.8626E+01	0.12
1	373.150	1.6606E+01	1.6646E+01		0.24	1.6691E+01	0.51
1	393.150	1.0178E+01	1.0336E+01		1.55	1.0293E+01	1.13
1	413.150	6.6420E+00	6.7210E+00		1.19	6.6490E+00	0.09
1	433.150	4.5048E+00	4.5330E+00		0.62	4.4636E+00	-0.91
1	453.150	3.1409E+00	3.1428E+00		0.06	3.0944E+00	-1.48
1	473.150	2.2029E+00	2.2215E+00		0.84	2.2010E+00	-0.08
1	493.150	1.5576E+00	1.5865E+00		1.86	1.5958E+00	2.45
1	513.150	1.0943E+00	1.1313E+00		3.37	1.1706E+00	6.97
1	533.150	7.5254E-01	7.8834E-01		4.76	8.6069E-01	14.37
1	553.150	4.7057E-01	5.0339E-01		6.97	6.2503E-01	32.82
AVG DEV					2.01		5.54

TABLE 5. SUMMARY OF COMPARISON OF COR AND PHC EQS. WITH PVT DATA

Substance	No. of Data	Temp. Range, K	Pres. Range, MPa	Vol. COR	Dev. Ave %		Data Source
					PHC		
Ethane	84	248/623	1.4/39	1.31	4.22		Douslin and Harrison in Goodwin et al. (1976)
Propane	81	311/511	0.55/69	0.66	2.18		Reamer in Goodwin (1977)
Propane	21	166/321	0.70/41	0.26	0.57		Ely in Goodwin (1977)
n-Butane	48	311/511	1.7/69	0.89	1.92		Olds in Goodwin (1979)
n-Octane	41	245/548	0.10/30	0.69	2.14		Felsing et al. (1942); Chappelow et al. (1972)
CO ₂	49	277/511	1.4/69	1.77	4.06		Sage and Lacey (1955)

TABLE 6. DETAILED COMPARISON OF COR AND PHC EQS. WITH pVT DATA FOR ETHYLENE

ρ gmol/dm ³	t , °C	COR		PHC		ρ gmol/dm ³	t , °C	COR		PHC		
		P , bar	% Dev	P , bar	% Dev			P , bar	% Dev	P , bar	% Dev	
0.8	-25	13.968	0.47	14.092	1.4	10.0	75	135.70	1.8	138.28	3.7	
	10	16.564	-0.14	16.774	1.1		150	227.15	-0.88	241.88	5.6	
	75	21.365	-0.16	21.642	1.1		10	55.057	4.7	43.189	-18.0	
	150	26.826	-0.05	27.159	1.2		75	175.73	2.2	173.18	0.76	
1.5	-25	22.395	1.5	22.819	3.4	11.0	150	315.89	0.74	326.11	4.0	
	10	27.594	-0.32	28.368	2.5		10	58.924	5.0	43.782	-22.0	
	75	37.318	-0.49	38.321	2.2		75	204.69	1.8	199.33	-0.89	
	150	48.258	-0.36	49.506	2.2		150	378.77	1.8	382.89	2.9	
3.5	0	41.237	0.61	44.168	7.8	12.0	10	67.530	3.6	50.034	-23.0	
	75	72.396	-1.3	76.779	4.7		75	244.53	1.1	235.61	-2.6	
	150	101.91	-1.5	108.32	4.7		125	387.16	2.1	381.39	0.59	
	5.0	10	50.426	0.56	54.038		7.8	13.0	0	51.879	-1.4	32.332
5.0	75	93.167	-0.81	99.159	5.6	14.0	50	216.40	0.00	200.67	-7.3	
	150	139.31	-1.9	150.18	5.8		100	388.52	1.7	372.86	-2.4	
	6.5	10	52.225	2.0	53.45		4.4	0	77.200	-4.8	55.390	-32.0
	75	113.28	0.45	118.62	5.2		75	382.75	0.48	357.45	-6.2	
6.5	150	179.32	-1.6	193.31	6.0	15.0	0	124.08	-7.1	97.431	-27.0	
	7.5	10	52.706	2.7	50.797		-1.0	50	370.55	-1.3	335.44	-10.0
	75	127.78	1.4	131.46	4.3		15.5	-25	27.196	-30.0	0.199	-99.0
	150	209.97	-1.2	224.77	5.8		0	159.03	-7.7	127.93	-26.0	
8.0	10	52.900	3.0	49.093	-4.4	30	320.81	-3.3	283.00	-15.0		

TABLE 7. SUMMARY COMPARISON OF EXPERIMENTAL AND COR EQ. CALCULATED K-VALUES

System (1) (2)	No. of Data Points	temp. Range, K	Pres. Range, bar	k ₁₂	av. abs. dev. (%)		Data Source
					K ₁	K ₂	
Methane + propane	40	277/361	7/99	0.053	1.9	0.78	Reamer et al. (1950)
Methane + neopentane	18	344/411	21/119	0.128	2.4	2.7	Prodany et al. (1971)
Methane n-decane	28	423/583	30/184	0.256	1.0	1.1	Lin et al. (1979)
Methane + benzene	18	421/501	19/239	0.081	4.3	7.0	Lin et al. (1979)
Ethane + n-heptane	32	339/450	31/84	0.101	1.8	5.5	Mehra et al. (1965)
n-butane-n-decane	61	311/511	1.7/48	0.077	2.3	7.0	Reamer et al. (1964)
Benzene(1)-cyclohexane	14	313/343	0.24/0.80	0.021	0.58	0.43	Scatchard (1939)
N ₂ + CO ₂	28	218/273	13/137	-0.032	7.3	2.3	Senner et al. (1963)
N ₂ + n-hexane	51	311/444	17/34	0.193	3.4	11.0	Poston et al. (1966)
CO + n-octane	17	463/533	6.8/54	0.224	1.6	3.0	Connolly (1965)
CO ₂ (1) + H ₂ S	32	273/353	20/80	0.071	4.9	0.78	Bierlein et al. (1953)
CO ₂ + ethane	45	223/283	6/62	0.102	1.8	2.0	Fredenslund et al. (1974)
CO ₂ + n-decane	16	463/584	19/50	0.263	2.1	2.8	Sebastian et al. (1980)
H ₂ S + ethane	45	200/283	1.3/30	0.071	3.3	6.6	Kalra et al. (1977)

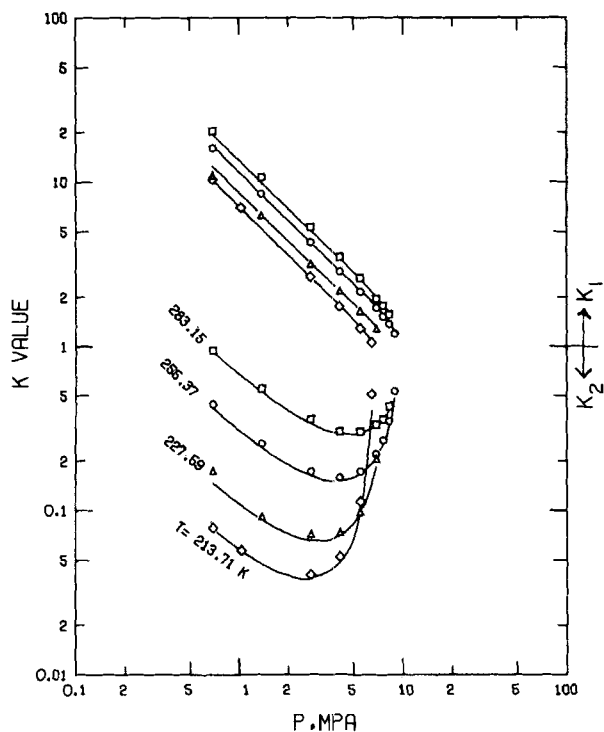


Figure 8. K -values for methane (1) + propane (3).

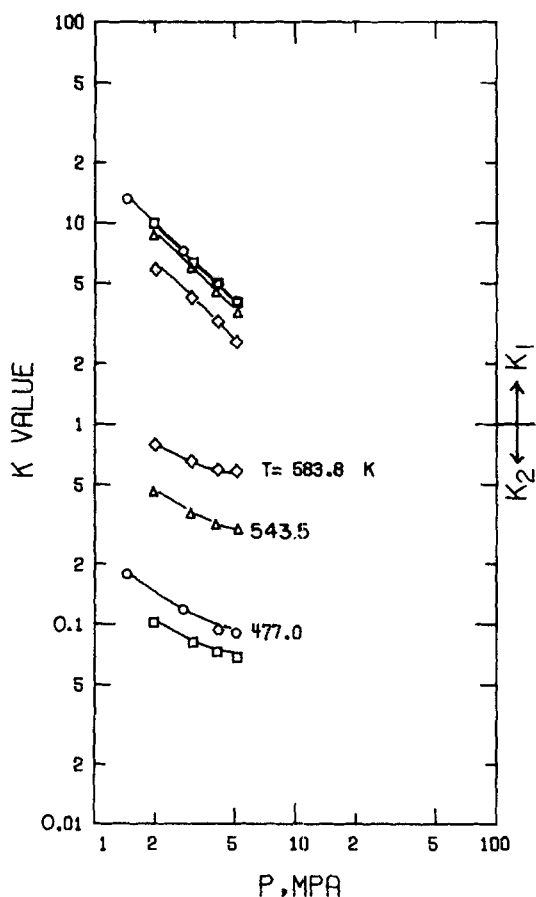


Figure 9. K -values for CO_2 (1) + n -decane (2).

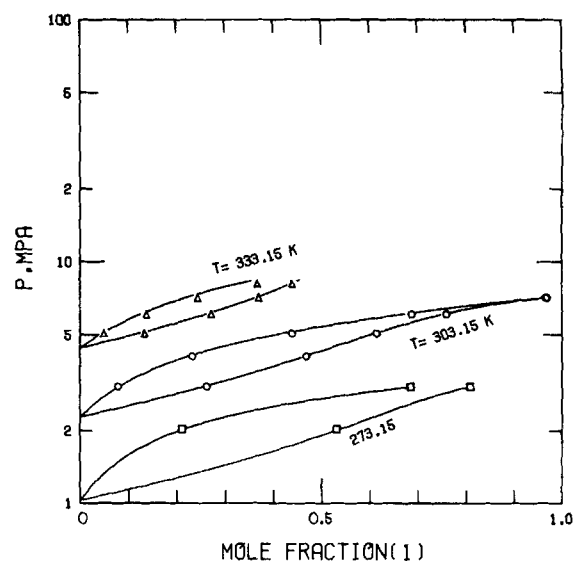


Figure 10. Bubble and dew pressures of CO_2 (1) + H_2S (2) mixtures.

equation contains only three constants for each substance, this application is relatively straightforward.

Van der Waals' one fluid mixing rules (1900) are in wide use. Leland (1968) found them to be superior to a number of other rules when applied to soft spheres and to molecules of different sizes. Smith (1971, 1972) introduced four exponents to generalize the mixing rules. Plöcker et al. (1978) and Radosz et al. (1982) retained one fractional exponent at the expense of substantially increased computations in following Smith's suggestion. In view of the considerable complexity of the COR equation itself, we use the van der Waals one fluid mixing rules as follows,

$$u_m V_{0m} = \sum_i \sum_j x_i x_j u_{ij} V_{0ij} \quad (20)$$

$$V_{0m} = \sum_i \sum_j x_i x_j V_{0ij} \quad (21)$$

where the doubly subscripted quantities are given by

$$u_{ii} = u_i \quad (22)$$

$$V_{0ii} = V_{0i} \quad (23)$$

in case $i = j$; and

$$u_{ij} = (1 - k_{ij}) \sqrt{u_i u_j} \quad (24)$$

$$V_{0ij} = (V_{0i} + V_{0j})/2 \quad (25)$$

in case $i \neq j$. Equation 24 contains an adjustable binary interaction parameter k_{ij} . Combining Eqs. 21 and 25 we obtain the simple additivity of V_{0m} ,

$$V_{0m} = \sum_i x_i V_{0i} \quad (26)$$

which satisfies Huron and Vidal's (1979) condition for finiteness of excess Gibbs energy at the limit of infinite pressure.

For c_m , we introduce a linear additivity rule.

$$c_m = \sum_i x_i c_i \quad (27)$$

From c_m and u_m we find T_m^* by solving Eq. 12.

$$T_m^* = \frac{-(1 + B_0 c_m/2) + \sqrt{(1 + B_0 c_m/2)^2 + 4B_1 c_m/2 \left(\frac{u_m}{kT} - B_2 c_m/2 \right)}}{c_m B_1/T} \quad (28)$$

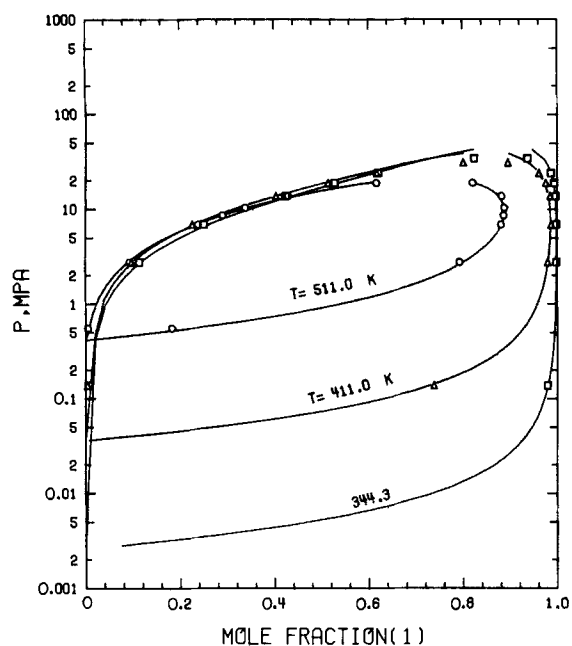


Figure 11. Bubble and dew pressures of methane (1) + n-decane (2) mixtures

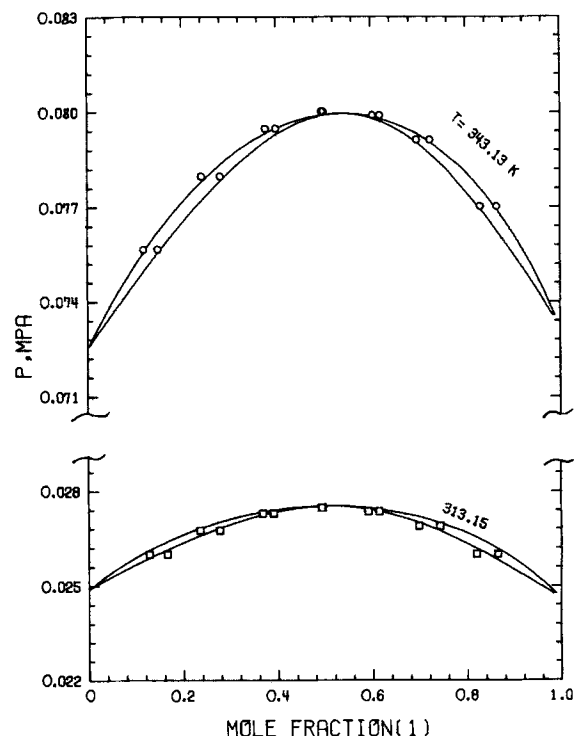


Figure 12. Bubble and dew pressures of benzene (1) + cyclohexane (2).

The reducing temperature of a mixture is temperature dependent.

From V_{om} of Eq. 26 and T_m^* of Eq. 28, we form the reduced quantities \tilde{v} and \tilde{T} for mixtures for use in the pressure equation, Eq. 15. The fugacity f_i of component i in a mixture is given by

$$\ln \frac{f_i}{x_i p} = -\ln \frac{pV}{nRT} + \frac{4 \frac{\tilde{v}}{\tau} - 3}{\left(\frac{\tilde{v}}{\tau} - 1\right)^2} - \frac{c_i}{2} \times (\alpha - 1) \left[(\alpha + 1) \ln \left(\frac{\frac{\tilde{v}}{\tau}}{\frac{\tilde{v}}{\tau} - 1} \right) - \frac{(\alpha + 4) \frac{\tilde{v}}{\tau} - 3}{\left(\frac{\tilde{v}}{\tau} - 1\right)^2} \right] + \left[1 + \frac{c_i}{2} (B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_{nm} \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} + \left(\frac{pV}{nRT} - 1 \right) \frac{V_{oi}}{V_{om}} + \left[\frac{c_m}{2} (-B_1/\tilde{T} + B_2\tilde{T}) \sum_{nm} \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} - \left[1 + \frac{c_m}{2} (B_0 + B_1/\tilde{T} + B_2\tilde{T}) \right] \sum_{nm} \frac{n A_{nm}}{\tilde{T}^n \tilde{v}^m} \right] \times \frac{\left[1 + \frac{c_i}{2} (B_0 + B_1/\tilde{T} + B_2\tilde{T}) - \tilde{T} \left(2 \sum_j x_j \frac{U_{ij} V_{oij}}{kT} - \frac{U_m V_{oi}}{kT} \right) \frac{1}{V_{om}} \right]}{\left[1 + \frac{c_m}{2} (B_0 + 2B_1/\tilde{T}) \right]} \quad (29)$$

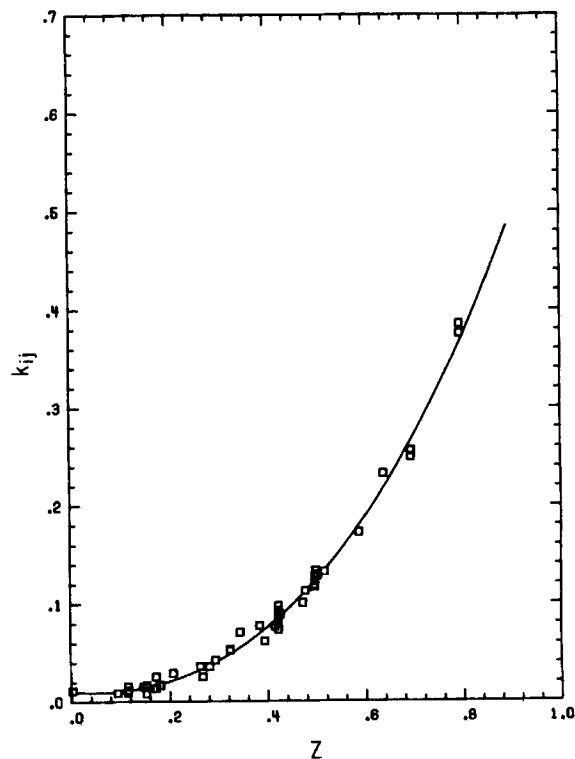


Figure 13. Correlation of k_{ij} hydrocarbon + hydrocarbon systems.

SOME MIXTURE SYSTEMS

We have studied some mixture systems of common interest using the COR equation including symmetric mixtures of nearly equally volatile components as well as asymmetric mixtures of greatly divergent components. For each binary mixture system, a value of the k_{ij} interaction parameter is determined for the best representations of the K -values. Table 7 presents the k_{ij} parameter, the temperature and pressure ranges of the experimental data and the average absolute deviation of calculated K -values for 14 binary systems. Similar results have been given by Chien (1981) for about 100 binary systems. Figures 8 and 9 show detailed comparison of some calculated K -values with experimental data. The larger deviations are observed at relatively low temperatures where the liquid-phase mole fractions of the light component and the vapor-phase mole fractions of the heavy component are small. Higher than usual experimental uncertainties should be expected for these small mole fractions.

Figures 10 and 11 show detailed comparison of isothermal $p - x/y$ relations. The COR equation gives generally good results except at conditions very close to the critical states.

Figure 12 shows the close agreement of the equation calculations with experimental data for the close-boiling benzene + cyclohexane mixtures. The azeotrope is well described.

The k_{ij} interaction parameters that we have determined have been found to correlate with the core volumes of the components in terms of the ratio Z defined as follows,

$$Z = |V_{O_i} - V_{O_j}| / (V_{O_i} + V_{O_j}) \quad (30)$$

For hydrocarbon + hydrocarbon mixtures the correlation is expressed by

$$k_{ij} = 0.01008 - 0.03429Z + 0.3849Z^2 + 0.2823Z^3 \quad (31)$$

and is shown in Figure 13.

For carbon monoxide + hydrocarbon mixtures

$$k_{ij} = 0.0315 - 0.1033Z + 0.5892Z^2 \quad (33)$$

ACKNOWLEDGMENT

Financial support of this work was provided by National Science Foundation through Grant 7912455A2 and Electric Power Research Institute through research project RP-367.

NOTATION

A_{nm}	= universal constants in Eq. 11
B	= second virial coefficient
B_0, B_1, B_2	= constants in Eq. 12
c	= rotational degrees of freedom
f	= fugacity
H	= enthalpy
k	= Boltzmann constant
k_{ij}	= binary energy interaction parameter
L	= ratio of l to σ
ℓ	= spheres' center to center distance in a hard dumbbell
N	= number of molecules
n	= number of moles
p	= pressure
Q	= canonical partition function
q	= canonical partition function per molecule
R	= gas constant
S	= entropy
T	= temperature
T^*	= characteristic temperature
\bar{T}	= reduced temperature
U	= internal energy
u	= characteristic energy
V	= total volume

V_o	= closest packed volume
\tilde{v}	= reduced volume
x	= mole fraction
Z	= variable defined in Eq. 30
Z	= compressibility factor

Greek Letters

α	= constant defined in Eq. 6
τ	= constant equal to $\pi\sqrt{2}/6$
σ	= hard sphere diameter

Subscripts

attr	= attractive contribution to Q
db	= hard dumbbell
i	= component i
j	= component j
m	= mixture
r	= rotational contribution
rep	= repulsive contribution to Q
t	= translational contribution

Superscript

$^\circ$	= ideal gas at 1 atm
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Manuscript received November 12, 1981; revision received August 31, and accepted September 3, 1982.