CHUE-PL 67-0590

$c(t)$ = concentration emerging from batch reactor after residence time t
D = coefficient of longitudinal diffusion
$f(t)$ = residence time distribution frequency function
$F(t)$ = integral residence time distribution
i = number of passages through recycle reactor
L = length of longitudinal diffusion reactor
n = number of CSTR's in series
n_p = integer above $\lambda_p(R + 1)/\theta$
Q = volumetric flow rate of feed
R = ratio of recycle flow to feed flow
t = time
u = axial velocity in longitudinal diffusion reactor
V = reactor volume
α = age of fluid element in reactor
$\bar{\alpha}$ = mean age
δ = delta function
θ = mean residence time V/Q
λ = life expectation of fluid element in reactor
λ_p = mean value of λ for a point
ξ = mean age of fluid elements with life expectation λ
$\rho(c)$ = rate of chemical reaction at concentration c
σ^2 = variance
$\psi(\lambda)$ = life expectation distribution frequency function
var α = variance of age of fluid elements in reactor
var α_p = variance of age between points
var α_I = variance of age within points

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VAPOR-LIQUID EQUILIBRIA AT HIGH PRESSURES. VAPOR-PHASE FUGACITY COEFFICIENTS IN NONPOLAR AND QUANTUM-GAS MIXTURES

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Vapor-phase fugacity coefficients, calculated with the Redlich-Kwong equation, are in excellent agreement with experimental results when Redlich's original mixing rule for constant *a* is modified by inclusion of one binary interaction constant. Such constants are reported here for 115 binary systems including several which contain hydrogen, neon, or helium. Quantum corrections for these gases are taken into consideration. The calculations are readily performed with an electronic computer and are useful for reduction and correlation of vapor-liquid equilibrium data at high pressures.

THERMODYNAMIC reduction and correlation of vapor-liquid equilibrium data are common at low pressures, but despite a generous supply of equilibrium data at high pressures, little attempt has been made to reduce such data with thermodynamically significant functions.

In high-pressure phase equilibria it is not possible to make various simplifying assumptions commonly made at low pressures and, as a result, thermodynamic analysis has only rarely been applied to high-pressure systems. In such systems, both phases, vapor and liquid, exhibit large deviations from ideal behavior. In previous papers we considered the liquid phase (Chueh *et al.*, 1965, 1967*B*) but in this work we consider the vapor phase; we are concerned with a reliable technique for calculating vapor-phase fugacity coefficients in nonpolar mixtures, including those containing one of the quantum gases. Toward that end we propose to use the Redlich-Kwong equation with certain modifications. Since we wish to use our technique in a computer program as a subroutine for calculation of K factors at high pressures, we prefer to use an analytical equation of state rather than the previously described corresponding-states method for estimating gas-phase properties (Gunn *et al.*, 1966; Prausnitz and Gunn, 1958).

The Redlich-Kwong equation is now nearly 20 years old; recently it has been discussed by several authors (Barner *et al.*, 1966; Estes and Tully, 1967; Robinson and Jacoby, 1965; Wilson, 1964), and it is generally regarded as the best two-parameter equation now available (Shah and Thodos, 1965). For mixtures, however, it often gives poor results, as does the recent modification given by Redlich and coworkers (1965). The failure of the equation to give consistently good results for mixtures is due to the inflexible mixing rules for the composition dependence of the equation-of-state constants. We present here a modified mixing rule for the constant a; this modification incorporates one characteristic binary constant and we report such constants for 115 binary systems. Extension to multicomponent systems follows without further assumptions and with no ternary (or higher) constants. A somewhat similar study, restricted to paraffin–carbon dioxide mixtures, has recently been published by Joffe and Zudkevitch (1966). Other modifications of the Redlich-Kwong equation have been reported by Wilson (1964), Estes and Tully (1967), Robinson and Jacoby (1965), and Barner, Pigford, and Shreiner (1966).

Fugacity Coefficient

The fugacity of a component i in a gas mixture is related to the total pressure, P, and its mole fraction, y_i, through the fugacity coefficient φ_i:

$$f_i = \varphi_i y_i P \tag{1}$$

The fugacity coefficient is a function of pressure, temperature, and gas composition; it is related to the volumetric properties of the gas mixture by either of the two exact relations (Beattie, 1949; Prausnitz, 1959):

$$RT \ln \varphi_i = \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP \tag{2}$$

$$RT \ln \varphi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \tag{3}$$

where V is the total volume of the gas mixture, and z is the compressibility factor of the gas mixture at T and P. Since most equations of state are explicit in pressure, Equation 3 is more convenient to use.

For a mixture of ideal gases $\varphi_i = 1$ for all i. For a gas mixture that follows Amagat's assumption ($\bar{v}_i = v_{\text{pure } i}$ at the same T and P for the entire pressure range from zero to P), Equation 2 gives the Lewis fugacity rule (Lewis and Randall, 1923) which says

$$\varphi_i = \varphi_{\text{pure } i} \quad \text{(at same } T \text{ and } P\text{)} \tag{4}$$

This simplifying assumption, however, may lead to large error, especially for components present in small concentrations. The Lewis fugacity rule becomes exact (at any pressure) only in the limit $y_i \rightarrow 1$.

The fugacity coefficient of component i in a gas mixture can be calculated from Equations 2 and 3 if sufficient volumetric data are available for the gas mixture. Since such data are not usually available, especially for multicomponent systems, fugacity coefficients are most often calculated by an extension of the theorem of corresponding states or with an equation of state. The method based on corresponding states has been discussed (Joffe, 1948; Leland *et al.*, 1962). In the following we discuss a method based on an equation of state which is more convenient to use than the corresponding-states method.

Equation of State

Only the virial equation has a sound theoretical foundation for representing the properties of pure and mixed gases. When truncated after the third term, the virial equation is useful up to a density nearly corresponding to the critical density. A method for estimating the third virial coefficient of mixtures is given elsewhere (Chueh and Prausnitz, 1967a,b; Orentlicher and Prausnitz, 1967). For application at higher densities, an empirical equation of state such as the Redlich-Kwong equation (1949) is more reliable. For vapor-phase fugacity coefficients we use the Redlich-Kwong equation throughout the entire range of density.

The Redlich-Kwong equation is

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5} v(v + b)} \tag{5}$$

where

$$a = \frac{\Omega_a R^2 T_{ci}^{2.5}}{P_{ci}} \tag{6}$$

$$b = \frac{\Omega_b R T_{ci}}{P_{ci}} \tag{7}$$

The dimensionless constants Ω_a and Ω_b are, respectively, 0.4278 and 0.0867 if the first and second isothermal derivatives of pressure with respect to volume are set equal to zero at the critical point. In vapor-liquid equilibria, however, we are interested in the volumetric behavior of saturated vapors over a relatively wide range of temperature, rather than in the critical region only. We propose, therefore, to evaluate Ω_a and Ω_b for each pure component by fitting Equation 5 to the volumetric data of the saturated vapor. The temperature range used is that from the normal boiling point to the critical temperature. Table I lists Ω_a and Ω_b for the saturated vapors of 19 pure substances most often encountered in high pressure vapor-liquid equilibria.

To apply Equation 5 to mixtures, we need a mixing rule. We propose

$$b = \sum_{i=1}^{N} y_i b_i \tag{8}$$

where

$$b_i = \frac{\Omega_{b_i} R T_{ci}}{P_{ci}} \tag{9}$$

and

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii} a_{jj}}) \tag{10}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{ci}^{2.5}}{P_{ci}} \tag{11}$$

$$a_{ij} = \frac{(\Omega_{a_i} + \Omega_{a_j}) R^2 T_{cij}^{2.5}}{2 P_{cij}} \tag{12}$$

$$P_{cij} = \frac{z_{cij} R T_{cij}}{v_{cij}} \tag{13}$$

Table I. Acentric Factors and Dimensionless Constants in Redlich-Kwong Equation of State for Saturated Vapors

	ω	Ω_a	Ω_b
Methane	0.013	0.4278	0.0867
Nitrogen	0.040	0.4290	0.0870
Ethylene	0.085	0.4323	0.0876
Hydrogen sulfide	0.100	0.4340	0.0882
Ethane	0.105	0.4340	0.0880
Propylene	0.139	0.4370	0.0889
Propane	0.152	0.4380	0.0889
Isobutane	0.187	0.4420	0.0898
Acetylene	0.190	0.4420	0.0902
1-Butene	0.190	0.4420	0.0902
n-Butane	0.200	0.4450	0.0906
Cyclohexane	0.209	0.4440	0.0903
Benzene	0.211	0.4450	0.0904
Isopentane	0.215	0.4450	0.0906
Carbon dioxide	0.225	0.4470	0.0911
n-Pentane	0.252	0.4510	0.0919
n-Hexane	0.298	0.4590	0.0935
n-Heptane	0.349	0.4680	0.0952
n-Octane	0.398	0.4760	0.0968

Table II. Characteristic Constant k_{12} for Binary Systems

$$\left[k_{12} = 1 - \frac{T_{c_{12}}}{(T_{c_{11}}T_{c_{22}})^{1/2}}\right]$$

System		$k_{12} \times 10^2$
1	2	
Methane	Ethylene	1
	Ethane	1
	Propylene	2
	Propane	2
	n-Butane	4
	Isobutane	4
	n-Pentane	6
	Isopentane	6
	n-Hexane	8
	Cyclohexane	8
	n-Heptane	10
	n-Octane	(12)[a]
	Benzene	(8)
	Toluene	(8)
	Naphthalene	14
Ethylene (or ethane)	Ethane	0
	Propylene	0
	Propane	0
	n-Butane	1
	Isobutane	1
	n-Pentane	2
	Isopentane	2
	n-Hexane	3
	Cyclohexane	3
	n-Heptane	4
	n-Octane	(5)
	Benzene	3
	Toluene	(3)
	Naphthalene	8
Propylene (or propane)	Propane	0
	n-Butane	0
	Isobutane	0
	n-Pentane	1
	Isopentane	0
	n-Hexane	(1)
	Cyclohexane	(1)
	n-Heptane	(2)
	n-Octane	(3)
	Benzene	2
	Toluene	(2)
n-Butane (or isobutane)	Isobutane	0
	n-Pentane	0
	Isopentane	0
	n-Hexane	0
	Cyclohexane	0
	n-Heptane	0
	n-Octane	(1)
	Benzene	(1)
	Toluene	(1)
n-Pentane (or isopentane)	Isopentane	0
	n-Hexane	0
	Cyclohexane	0
	n-Heptane	0
	n-Octane	0
	Benzene	(1)
	Toluene	(1)
n-Hexane (or cyclohexane)	*n*-Heptane	0
	n-Octane	0
	Benzene	(1)
	Toluene	1
n-Heptane	*n*-Octane	0
	Benzene	(1)
	Toluene	(1)
n-Octane	Benzene	(1)
	Toluene	(1)
Benzene	Toluene	(0)
Carbon dioxide	Methane	(5 ± 2)
	Ethylene	6
	Ethane	8
	Propylene	10
	Propane	11 ± 1
	n-Butane	16 ± 2
	Isobutane	(16 ± 2)
	n-Pentane	(18 ± 2)
	Isopentane	(18 ± 2)
	Naphthalene	24
Hydrogen sulfide	Methane	5 ± 1
	Ethylene	(5 ± 1)
	Ethane	6
	Propylene	(7)
	Propane	8
	n-Butane	(9)
	Isobutane	(9)
	n-Pentane	11 ± 1
	Isopentane	(11 ± 1)
	Carbon dioxide	8
Acetylene	Methane	(5)
	Ethylene	6
	Ethane	8
	Propylene	7
	Propane	9
	n-Butane	(10)
	Isobutane	(10)
	n-Pentane	(11)
	Isopentane	(11)
Nitrogen	Methane	3
	Ethylene	4
	Ethane	5
	Propylene	(7)
	Propane	(9)
	n-Butane	12
	Helium	16
Argon	Methane	2
	Ethylene	3
	Ethane	3
	Oxygen	1
	Nitrogen	0
	Helium	5 ± 1
Tetrafluoromethane	Methane	7
	Nitrogen	2
	Helium	(16 ± 2)
Hydrogen	Methane	3
Neon	Methane	28
	Krypton	20 ± 2
Krypton	Methane	1

[a] *Numbers in parentheses are interpolated or estimated values.*

$$v_{c_{ij}}^{1/3} = \frac{1}{2}\left(v_{c_i}^{1/3} + v_{c_j}^{1/3}\right) \tag{14}$$

$$z_{c_{ij}} = 0.291 - 0.08\left(\frac{\omega_i + \omega_j}{2}\right) \tag{15}$$

$$T_{c_{ij}} = \sqrt{T_{c_{ij}}T_{c_{ij}}}(1 - k_{ij}) \tag{16}$$

The binary constant k_{ij} represents the deviation from the geometric mean for $T_{c_{ij}}$. It is a constant characteristic of the *i-j* interaction; to a good approximation, k_{ij} is independent of the temperature, density, and composition. In general, k_{ij} must be obtained from some experimental information about the binary interaction. Good sources of this information are provided by second virial cross coefficients (Prausnitz, and Gunn, 1958) or by saturated liquid volumes of binary systems (Chueh and Prausnitz, 1967b), Table II presents our best estimates of k_{ij} for 115 binary systems. As new experimental data become available, this table should be revised and enlarged.

The proposed mixing rule for a_{ij} differs from Redlich's original mixing rule in two respects: (1) introduction of a binary constant k_{ij}, and (2) combination of critical volumes and compressibility factors to obtain a_{ij} according to Equations 12 through 15. As a result of (2), the proposed mixing rule does not reduce to Redlich's original rule even when $k_{ij} = 0$, except when v_{c_i}/v_{c_j} is close to unity; in general, Redlich's original rule gives a value for a_{ij} slightly smaller than that given by the proposed rule with $k_{ij} = 0$. For example, for the methane–n-pentane system, Redlich's original rule gives $a_{ij} = 5.80 \times 10^5$ (p.s.i.a.) (° R.)$^{0.5}$ (cu. ft./lb. mole)^2, whereas the proposed rule gives 6.26×10^5 with $k_{ij} = 0$, and 5.70×10^5 with the recommended k_{ij} of 0.06. For this particular case, Redlich's original rule gives a value of a_{ij} close to that of the proposed rule with the recommended k_{ij} (as obtained from second virial cross coefficients). On the other hand, for the system ethane-acetylene, for which v_{c_i}/v_{c_j} is nearly unity, Redlich's original rule gives an a_{ij} which is essentially equal to that given by the proposed rule with $k_{ij} = 0$; such a_{ij} is 12% too large as compared to the a_{ij} given by the proposed rule with a recommended k_{ij} of 0.08. Finally, for the system carbon dioxide–n-butane, a_{ij} from Redlich's original rule corresponds to that of the proposed rule with $k_{ij} = 0.04$, as compared to a k_{ij} of 0.18 obtained from second virial cross coefficients. This may explain why Redlich's original rule often works well for paraffin-paraffin systems but not for systems containing chemically dissimilar components.

Fugacity Coefficients from Revised Redlich-Kwong Equation

By substituting Equation 5 and the mixing rules, Equations 8 to 16, into Equation 3, the fugacity coefficient of component k in the mixture becomes

$$\ln \varphi_k = \ln \frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2 \sum_{i=1}^{N} y_i a_{ik}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_k}{RT^{3/2}\, b^2}\left[\ln \frac{v+b}{v} - \frac{b}{v+b}\right] - \ln \frac{Pv}{RT} \quad (17)$$

The molar volume, v, is that of the gas mixture; it is obtained by solving Equation 5 (which is cubic in v) and taking the largest real root for v.

Figure 1 shows experimental and calculated compressibility factors for three mixtures of nitrogen and n-butane at 310° F. (Evans and Watson, 1956). The values of Ω_a and Ω_b used are those for the pure saturated vapors, although the gas mixtures at this temperature are actually supercritical. The calculated compressibility factors for the gas mixture are in good agreement with the experimental data up to a pressure as high as 9000 p.s.i.a.

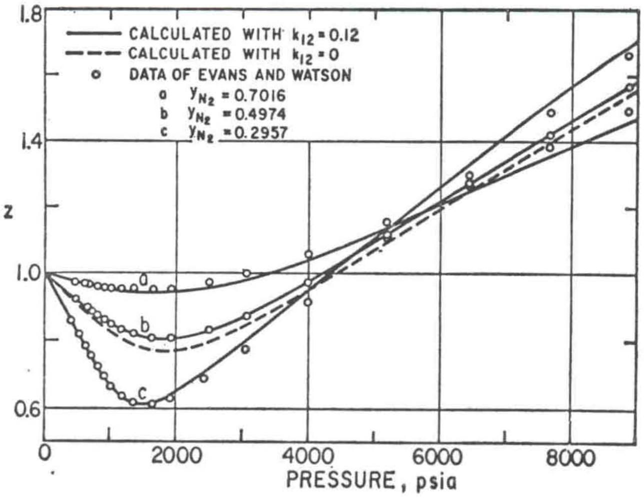

Figure 1. Compressibility factors of nitrogen–n-butane mixtures at 310° F.

$k_{12} = 0.12$ obtained from second virial coefficient data

Figure 2 shows experimental and calculated fugacity coefficients of carbon dioxide in a mixture containing 85 mole % n-butane at 340° F. The experimental fugacity coefficients of carbon dioxide are obtained from the volumetric data of Olds *et al.* (1949) by performing graphically the differentiation and integration indicated in Equation 2. The test is a rather stringent one, since the mole fraction of carbon dioxide is small and the gas mixture is near its critical temperature. The fugacity coefficient of carbon dioxide shows an unusual pressure dependence, going through two inflections and a sharp maximum. The agreement is good considering the uncertainty involved in the numerical differentiation of the experimental data. Also indicated is the poor result obtained when the geometric mean assumption is used for $T_{c_{12}}$. The Lewis fugacity rule fails badly at all pressures, since the mole fraction of carbon dioxide is small.

Figure 3 shows experimental and calculated fugacity coefficients of ethane in an equimolar mixture with methane. The experimental fugacity coefficients of ethane are those reported by Sage and Lacey (1950). Figures 4, 5, and 6 show experimental and calculated compressibility factors for saturated vapor mixtures of three binary systems: propane-methane (Reamer *et al.*, 1950), n-pentane–methane (Sage *et al.*, 1942), and n-pentane–hydrogen sulfide (Reamer *et al.*, 1953). Compressibility factors of the saturated vapors of the first two binary systems first increase with rising methane concentration but soon decrease because of the effect of high pressure. The calculated compressibility factors reproduce this behavior. The agreement is good except for the n-pentane–methane system near the critical.

For the n-pentane–hydrogen sulfide system at 160° F., both components are subcritical and the experimental and calculated compressibility factors are in good agreement over the entire composition range, from pure n-pentane to pure hydrogen sulfide. Calculations based on Redlich's original mixing rules (Redlich and Kwong, 1949) show less satisfactory agreement with experimental data. Also shown are the calculated fugacity coefficients for the heavy components; the fugacity coefficients of propane and n-pentane at high pressure and low

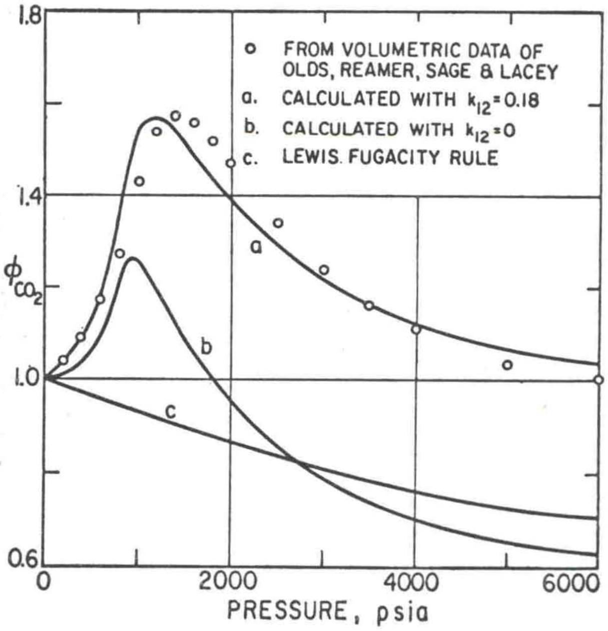

Figure 2. Fugacity coefficients of carbon dioxide in a mixture containing 85 mole % n-butane at 340° F.

$k_{12} = 0.18$ obtained from second virial coefficient data

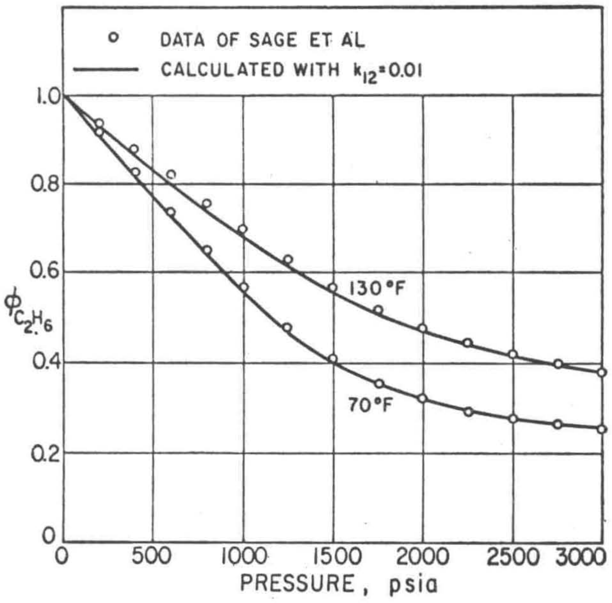

Figure 3. Fugacity coefficients of ethane in an equimolar mixture with methane

k_{12} = 0.01 obtained from second virial coefficient data

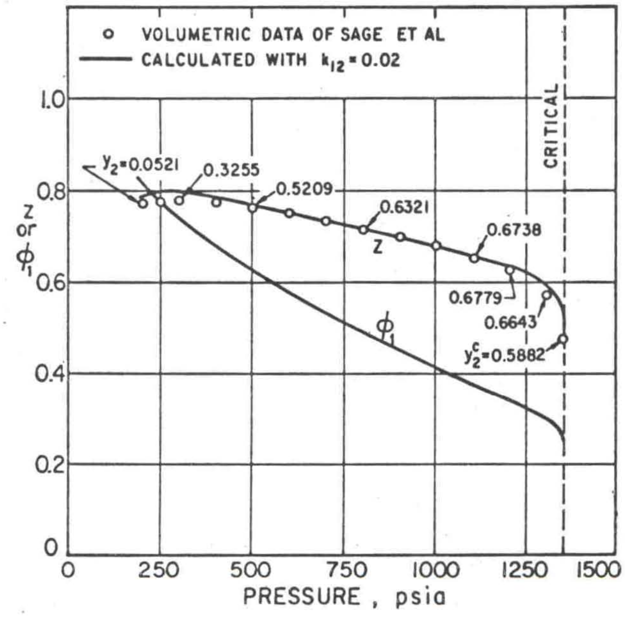

Figure 4. Compressibility factors and fugacity coefficients for saturated vapor of propane (1)–methane (2) system at 100° F.

k_{12} = 0.02 obtained from saturated liquid volume data

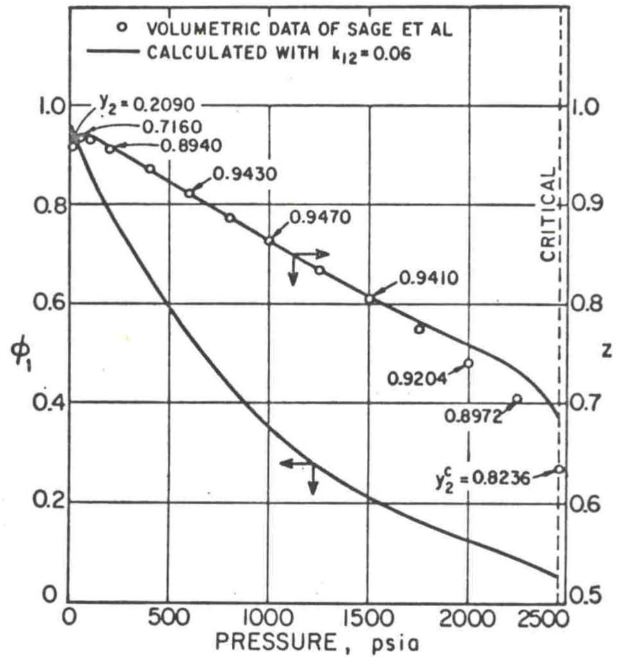

Figure 5. Compressibility factors and fugacity coefficients for saturated vapor of *n*-pentane (1)–methane (2) system at 100° F.

k_{12} = 0.06 obtained from saturated liquid volume data

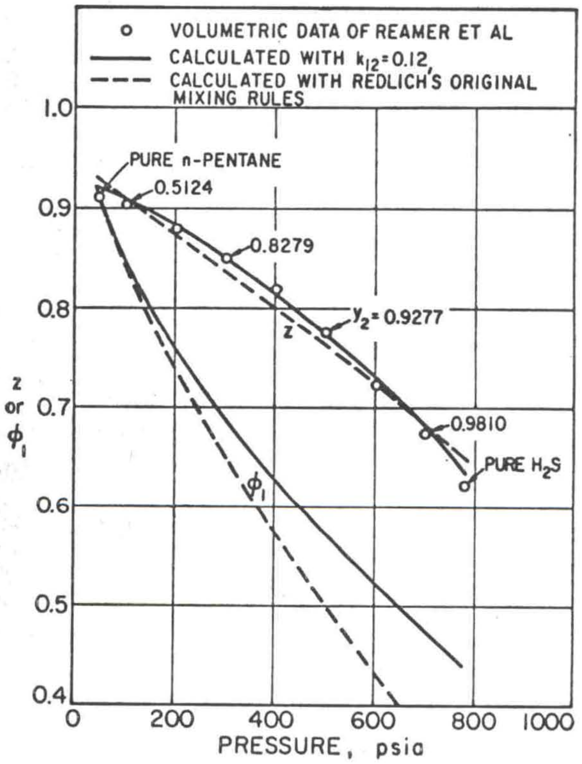

Figure 6. Compressibility factors and fugacity coefficients for saturated vapor of *n*-pentane (1)–hydrogen sulfide (2) at 160° F.

k_{12} = 0.12 obtained from second virial coefficient data

concentration are extremely small. These results indicate very large deviations from ideal-gas behavior and from the Lewis fugacity rule; they point to the need for serious consideration of vapor-phase imperfections in high-pressure vapor-liquid equilibria.

Quantum Gases

The configurational properties of low-molecular-weight gases (hydrogen, helium, neon) are described by quantum, rather than classical, statistical mechanics. As a result, the properties of these gases cannot be given by the same corresponding-states treatment (Equations 9, and 11 to 16) as that used for classical gases when the true critical constants are used as the reducing parameters. It is possible, however, to define temperature-dependent, effective critical constants (Gunn *et al.*, 1966) with which the properties of quantum gases can be made to coincide with those for classical gases. These effective critical constants were found to depend on the molecular mass, m, and temperature in a simple manner. The effective critical temperature and effective critical pressure are given by

$$T_c = \frac{T_c^\circ}{1 + \frac{c_1}{mT}} \tag{18}$$

$$P_c = \frac{P_c^\circ}{1 + \frac{c_2}{mT}} \tag{19}$$

where

$$c_1 = 21.8^\circ \text{ K.} \tag{20}$$

$$c_2 = 44.2^\circ \text{ K.} \tag{21}$$

T_c° and P_c° are, respectively, the classical critical temperature and pressure—i.e., the effective critical temperature and pressure in the limit of high temperature. Table III gives T_c° and P_c° for nine quantum gases.

For mixtures containing one or more of the quantum gases, Equations 8 through 12 are used, except that T_{c_i} and P_{c_i} are given by Equations 18 and 19; further, $T_{c_{ij}}$ and $P_{c_{ij}}$ are given by

$$T_{c_{ij}} = \frac{\sqrt{T^\circ_{c_{ii}} T^\circ_{c_{jj}}}\,(1 - k_{ij})}{1 + \frac{c_1}{m_{ij}T}} \tag{22}$$

$$P_{c_{ij}} = \frac{P^\circ_{c_{ij}}}{1 + \frac{c_2}{m_{ij}T}} \tag{23}$$

where

$$P^\circ_{c_{ij}} = \frac{z^\circ_{c_{ij}} R \sqrt{T^\circ_{c_{ii}} T^\circ_{c_{jj}}}\,(1 - k_{ij})}{v^\circ_{c_{ij}}} \tag{24}$$

$$v^{\circ\,1/3}_{c_{ij}} = \frac{1}{2}\left(v^{\circ\,1/3}_{c_i} + v^{\circ\,1/3}_{c_j}\right) \tag{25}$$

$$z^\circ_{c_{ij}} = 0.291 - 0.08\left(\frac{\omega_i + \omega_j}{2}\right) \tag{26}$$

$$\frac{1}{m_{ij}} = \frac{1}{2}\left(\frac{1}{m_i} + \frac{1}{m_j}\right) \tag{27}$$

For all quantum gases, Ω_a and Ω_b are, respectively, 0.4278 and 0.0867, and ω(effective) is zero. Values of v_c° for quantum gases are calculated from the relation $v_c^\circ = 0.291RT_c^\circ/P_c^\circ$; they are listed in Table III.

Figure 7 shows experimental and calculated compressibility factors for the two quantum gases, hydrogen (Johnston and White, 1948) and helium (Mann, 1962) at cryogenic temperatures. Calculated results were obtained from the Redlich-Kwong equation using effective critical constants. Good agreement is obtained over the entire temperature and pressure range, including the isotherms very close to the critical. The slightly high compressibility factors near the critical point are due to an inherent limitation of the Redlich-Kwong equation which gives $z_c = 1/3$ for all gases when $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$.

Table III. Classical Critical Constants for Quantum Gases

	T_c°, ° *K.*	P_c°, *Atm.*	v_c°, *Cc./Gram Mole*
Ne	45.5	26.9	40.3
He^4	10.47	6.67	37.5
He^3	10.55	5.93	42.6
H_2	43.6	20.2	51.5
HD	42.9	19.6	52.3
HT	42.3	19.1	52.9
D_2	43.6	20.1	51.8
DT	43.5	20.3	51.2
T_2	43.8	20.5	51.0

Figure 8 shows experimental and calculated fugacity co-

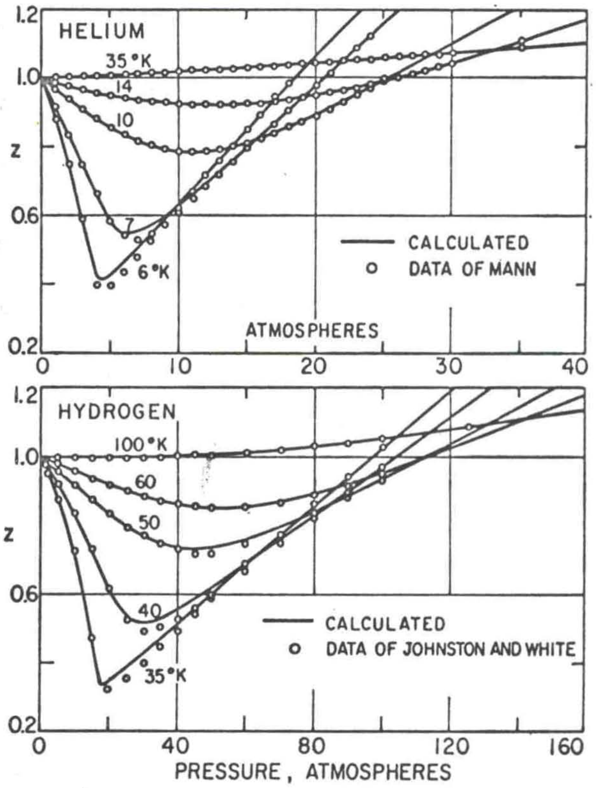

Figure 7. Compressibility factors of helium and hydrogen at low temperatures

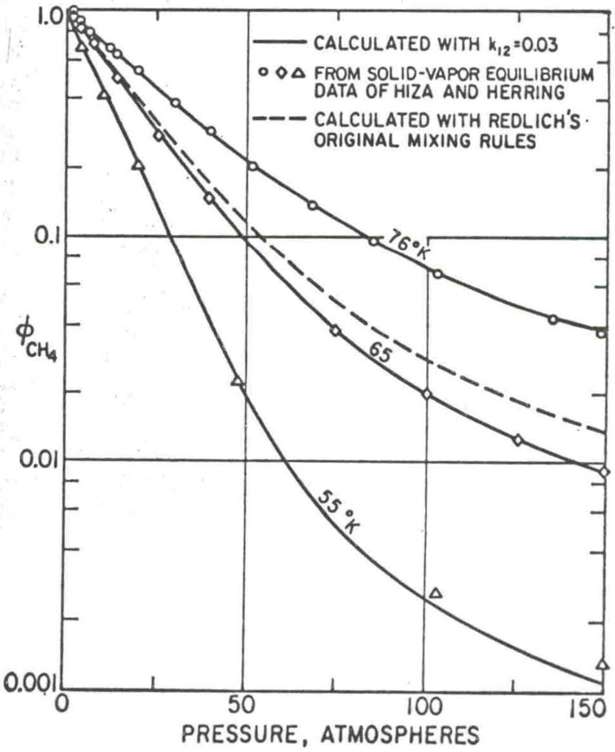

Figure 8. Fugacity coefficients of methane in hydrogen at saturation

k_{12} = 0.03 obtained from second virial coefficient data efficients of methane in a mixture with hydrogen at equilibrium with solid methane (Hiza and Herring, 1965). The good agreement at these low temperatures and high pressures suggests that the revised Redlich-Kwong equation can be successfully applied to mixtures of nonpolar and quantum gases.

Conclusion

The equation of Redlich and Kwong provides a simple method for calculation of fugacity coefficients in nonpolar vapor mixtures at high pressures. The dimensionless constants Ω_a and Ω_b which are universal in the original Redlich-Kwong equation are replaced by constants evaluated from the saturated volumetric properties of each pure component. This modification is relatively unimportant for the vapor phase, although it is very important for the liquid phase (Chueh and Prausnitz, 1967b). The large improvement for vapor mixtures is obtained through a modification in the mixing rule for the equation-of-state constant, a; for mixtures, the accuracy of the equation is significantly increased when the original, inflexible mixing rule is replaced by a flexible rule which contains one characteristic binary constant. Through effective critical constants the equation of state can also be used for mixtures containing one or more of the quantum gases. Vapor-phase fugacity coefficients calculated by this modification of the Redlich-Kwong equation are useful for reduction and correlation of high-pressure phase equilibrium data (Chueh, 1967).

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Nomenclature

a, b = constants in Redlich-Kwong equation of state
c_1, c_2 = constants given by Equations 20 and 21
f = fugacity
k_{ij} = characteristic constant for i-j interaction
m = molecular weight
m_{ij} = molecular weight characteristic of i-j interaction; the reduced mass
N = number of components in the mixture
n_i = number of moles of component i
P = total pressure
P_c = critical pressure
P_c° = classical critical pressure (high-temperature limit of effective critical pressure)
P_{cij} = critical pressure characteristic of i-j interaction
R = gas constant
T = temperature
T_c = critical temperature
T_c° = classical critical temperature (high-temperature limit of effective critical temperature)
T_{cij} = critical temperature characteristic of i-j interaction
v = molar volume of vapor phase
v_c = critical volume
v_c° = classical critical volume ($v_c^\circ = 0.291RT_c^\circ/P_c^\circ$ for quantum gases)
v_{cij} = critical volume characteristic of i-j interaction
y = mole fraction
z = compressibility factor
z_c = critical compressibility factor
z_c° = classical critical compressibility factor (0.291 for quantum gases)
z_{cij} = critical compressibility factor characteristic of i-j interaction
ω = acentric factor
φ_i = fugacity coefficient of component i in a gas mixture
Ω_a, Ω_b = dimensionless constants in Redlich-Kwong equation

SUPERSCRIPT

$^\circ$ = classical

SUBSCRIPTS

c = critical
i, ii = pure component i
ij = i-j pair

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