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- 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.

HERMODYNAMIC 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.

= concentration emerging from batch reactor after

= residence time distribution frequency function

= number of passages through recycle reactor

= axial velocity in longitudinal diffusion reactor

= life expectation of fluid element in reactor

= rate of chemical reaction at concentration c

= mean age of fluid elements with life expectation λ

residence time t

= coefficient of longitudinal diffusion

= integral residence time distribution

= number of CSTR's in series

= integer above $\lambda_p(R+1)/\theta$

= volumetric flow rate of feed = ratio of recycle flow to feed flow

= age of fluid element in reactor

= mean residence time V/Q

= mean value of λ for a point

= length of longitudinal diffusion reactor

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, 1967B) 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

c(t)

D

i L

n

 $n_p Q R$

t

и V

α

 $\overline{\alpha}$

δ

θ λ

 λ_p

 $\rho(c)$

ξ

= time

= reactor volume

= delta function

= mean age

f(t)F(t)

an analytical equation of state rather than the previously described corresponding-states method for estimating gasphase 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 twoparameter 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