ent research:

1. Theoretical rate equations have been derived for liquid phase mass transfer accompanied by first-order complex chemical reactions. The kinetics considered is a combination of consecutive, reversible, and parallel chemical reactions.
2. The film-penetration model has been shown to be a general model among the theories considered. It takes the film theory and the surface renewal theory as the lower and upper limits, respectively, in the theoretical predictions.
3. The ratio of chemical to physical mass transfer coefficients is smaller than that for mass transfer with a first-order irreversible reaction. The theories deviate significantly for cases where the reversible reaction is strong, and the diffusivities of the intermediate product and the reactant are quite different.

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NOTATION

C_A = concentration of component A, g.-mole/liter
C_{Ai} = concentration of component A at interphase, g.-mole/liter
C_{AL} = concentration of component A at the outer edge of a surface element, or in the liquid bulk, g.-mole/liter
C_E = concentration of component E, g.-mole/liter
C_{EL} = concentration of component E at the outer edge of a surface element, or in the liquid bulk, g.-mole/liter
D_A = molecular diffusivity of component A, sq.cm./sec.
D_E = molecular diffusivity of component E, sq.cm./sec.
D_{EA} = diffusivity ratio, D_E/D_A
K_1 = ratio of reaction rate constants k_{-1}/k_1
K_2 = ratio of reaction rate constants, k_2/k_1
K_3 = ratio of reaction rate constants, $\sum_{i=1}^{m} k_{1i}/k_1$
K_4 = ratio of reaction rate constants, $\sum_{j=1}^{n} k_{2j}/k_1$
L = average thickness of a surface element, or of a film, cm.
M = dimensionless group, $k_1 D_A/(k_L')^2$
$\overline{N}_A$ = average rate of chemical mass transfer for component A, g.-mole/(sq.cm.) (sec.)
k_r = first-order reaction rate constant, sec.$^{-1}$, $r = 1$, 11, 12, ... 1m, 2, 21, 22, . . . 2n, for forward reactions, $r = -1$ for backward reaction
k_L' = liquid side mass transfer coefficient without chemical reaction, cm./sec.
k_L = liquid side mass transfer coefficient with chemical reaction, cm./sec.
s = surface renewal rate, sec.$^{-1}$
t = time, sec.
χ = distance, cm.
γ = dimensionless group, D_A/sL^2

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Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State

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It was shown by us in a previous paper (*1*) that a modified Redlich-Kwong equation may be used to calculate both liquid-phase and vapor-phase fugacity coefficients of components in mixtures, provided that the dimensionless R-K parameters Ω_a and Ω_b of each pure component are first established from the P-V-T properties of the saturated liquid. The values of Ω_a and Ω_b were obtained at each of a series of temperatures by solving simultaneously the R-K equation

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \tag{1}$$

and

$$\ln \phi_L{}^s = \ln RT/P(V_l - b) + (PV_l/RT) - 1 - (a/RT^{3/2}b)\ln (V_l + b)/V_l \tag{2}$$

The values of the fugacity coefficient $\phi_L{}^s$ were obtained from the generalized correlation of Lyckman, Eckert, and Prausnitz (*2*). The R-K constants a and b are related to the dimensionless Ω_a and Ω_b parameters as follows:

$$a = \Omega_a R^2 T_c{}^{2.5}/P_c \tag{3}$$

$$b = \Omega_b R T_c/P_c \tag{4}$$

TABLE 1. SATURATED LIQUID PROPANE R-K PARAMETERS

Temperature °F.	Present method Ωa	Present method Ωb	Previous method Ωa	Previous method Ωb
−118.6	0.4205	0.08192	0.4205	0.08192
− 43.7	0.4273	0.08228	0.4283	0.08233
7.1	0.4258	0.08180	0.4274	0.08189
35.7	0.4238	0.08141	0.4258	0.08155
56.7	0.4216	0.08102	0.4241	0.08122
73.6	0.4195	0.08068	0.4226	0.08094
111.7	0.4138	0.07979	0.4187	0.08028
155.4	0.4046	0.07823	0.4136	0.07938
187.6	0.4007	0.07805	0.4151	0.08037
201.2	0.4036	0.07931	0.4208	0.08257

The coefficients Ω_a and Ω_b are dimensionless; their notation was introduced by Chueh and Prausnitz (*7, 8*).

In this approach, Ω_a and Ω_b are treated as temperature functions, an idea used by others: Wilson (*3, 4*); Robinson and Jacoby (*5*); and Barner, Pigford, and Schreiner (*6*). While the Ω_a and Ω_b parameters are determined here from saturated liquid-phase properties, the same parameters are employed for vapor-phase calculations. This procedure differs from that of Chueh and Prausnitz (*7, 8*) who treat Ω_a and Ω_b as constants and evaluate two different sets, one for the liquid and another for the vapor.

It is the objective of this communication to present a more recently developed alternative procedure for establishing the pure component Ω_a and Ω_b parameters as temperature functions. This alternative procedure utilizes the same saturated liquid properties, vapor pressure and volume, as the original procedure, but it dispenses with Lyckman's correlated values of $\phi_L{}^s$. This can be done because of the additional constraint introduced by forcing the equalization of the fugacity coefficients in the saturated vapor and the saturated liquid:

$$\phi_v{}^s = \phi_L{}^s \qquad (5)$$

An analogous procedure has been used before in reference to the BWR equation of state (*9*) and recently by Chang and Lu in the calculation of partial molal volumes of liquid mixtures (*10*).

The new method utilizes Equation (2) twice, once for the saturated liquid, as above, and again for the saturated vapor:

$$\ln \phi_v{}^s = \ln RT/P(V_g - b) + (PV_g/RT) - 1 - (a/RT^{3/2}b)\ln(V_g + b)/V_g \qquad (6)$$

By setting the right-hand sides of Equations (2) and (6) equal to each other and by utilizing Equations (3) and (4), the following relation is obtained:

$$\Omega_a = \Omega_b \left[\frac{\ln(V_g - b)/(V_l - b) - P(V_g - V_l)/RT}{(T_c/T)^{3/2} \ln V_g(V_l + b)/V_l(V_g + b)} \right] \qquad (7)$$

Equation (7) is solved simultaneously with Equation (1) at each temperature below the critical point to yield values of Ω_a and Ω_b. The solution must proceed by trial and error.

Procedure for simultaneous solution was developed and a computer program was written for its execution via the following steps:

1. Start with a trial value of Ω_b and with experimental values of T, P, and V_l. Solve Equation (1) for a and for Ω_a. This value of Ω_a may be designated as $\Omega_a I$.
2. Since a and b are now known, Equation (1) may be solved for the saturated vapor volume V_g. This requires solving the Redlich-Kwong equation by a trial-and-error procedure, such as the Newton-Raphson method, for its largest root.
3. The known values of V_g, V_l, P, T, and Ω_b are substituted into Equation (7), and Ω_a is found. This value of Ω_a is designated $\Omega_a II$. If $\Omega_a I$ and $\Omega_a II$ are found to be equal within a designated tolerance, then the trial value of Ω_b is correct and the solution is complete. If, however, $\Omega_a I$ and $\Omega_a II$ are not equal, a new trial value of Ω_b must be selected and the trial solution repeated. After the second trial, a simple convergence procedure, known as the secant method (*11*), is utilized in the computer program to converge on the desired solution, $\Omega_a II = \Omega_a I$.

In Table 1, the Ω values for saturated propane obtained by the fugacity equalization method are compared with those obtained by the method described in our previous

TABLE 2. COMPARISON OF EXPERIMENTAL AND CALCULATED K VALUES FOR THE SYSTEM METHANE-*n*-HEPTANE

Data by Reamer and Sage (*14*)
Binary Interaction Constant $C_{17} = -0.006$

Temp., °F.	Press., lb./sq.in.abs.	Component	Liquid-phase mole fr.	Experimental *K* const.	% deviation in *K* Previous method	% deviation in *K* Present method
100	1,000	C_1	0.2842	3.487	−3.52	−3.61
		C_7	0.7158	0.0126	−22.80	−22.27
100	3,000	C_1	0.6910	1.397	−0.21	−0.26
		C_7	0.3090	0.152	−5.83	−5.52
160	2,500	C_1	0.5580	1.719	−2.09	−2.18
		C_7	0.4420	0.093	−2.06	−1.58
220	200	C_1	0.0494	18.101	−4.67	−4.90
		C_7	0.9506	0.111	−1.56	−0.26
220	2,000	C_1	0.4457	2.126	−3.60	−3.77
		C_7	0.5543	0.095	0.57	1.47
340	1,500	C_1	0.3316	2.521	−5.14	−5.66
		C_7	0.6684	0.245	−1.74	−0.05
400	1,500	C_1	0.3725	1.863	0.74	0.06
		C_7	0.6275	0.488	−3.94	−2.65
400	1,750	C_1	0.4620	1.448	1.33	0.85
		C_7	0.5380	0.615	−2.69	−1.93
Average absolute % deviation		C_1			2.66	2.56
		C_7			5.15	4.47

TABLE 3. COMPARISON OF EXPERIMENTAL AND CALCULATED *K* VALUES FOR THE SYSTEM METHANE-ETHANE-PROPANE

Data by Price and Kobayashi (*15*)

Temperature range, °F.	Pressure range, lb./sq.in.abs.	Number of points tested	Average % Deviation in K	
			Previous method	Present method
−100 to 0	400 to 1,300	10		
Component 1	Methane		3.14	3.00
Component 2	Ethane		5.34	5.33
Component 3	Propane		4.82	4.40

Binary interaction constants:
$C_{12} = 0.009$, $C_{13} = 0.073$, $C_{23} = 0.027$

paper (*1*). The P-V-T data used in the calculations were taken from Din (*12*). It may be seen from insepection of the table that the effect of temperature on the values of the R-K parameters is qualitatively the same for the two methods. However, there is a numerical difference in the two sets of values of Ω_a and Ω_b, which can lead to different results when these parameters are used for calculating vapor-liquid *K* ratios via the procedure described in our previous paper (*1*).

It should be pointed out that the new procedure for establishing the values of Ω_a and Ω_b of a pure component, described in this communication, can only be used below the critical temperature of the component. At the critical point, Equation (7) becomes indeterminate. It is therefore necessary to use the original procedure of the previous paper (*1*) at the critical temperature to establish the values of Ω_a and Ω_b. At temperatures above the critical, Ω_a and Ω_b were treated as constants in the earlier work (*1*) and were assigned the same values as at the critical point. The same procedure is used in the current work at temperatures above the critical.

CALCULATION OF VAPOR-LIQUID EQUILIBRIUM *K* RATIOS

The calculation of *K* ratios with the R-K equation utilizing temperature-dependent R-K parameters has been described in our previous paper (*1*). For the calculation of *K* ratios in multicomponent mixtures, it is necessary to have not only R-K parameters for each pure component but also an interaction parameter C_{ij} for each binary pair in the mixture. It was found in the current work, in the case of several binary pairs tested, that the C_{ij} parameters previously established by us for these binaries (*1*) can also be used in the current work. No appreciable difference in the optimum C_{ij} values based on the old and new sets of R-K parameters has been observed. Accordingly, *K* ratios for several hydrocarbon binaries and one ternary system were calculated, based on new sets of R-K parameters but utilizing the same C_{ij} parameters as in our previous work (*1*). The resulting *K* values have been compared with those calculated by the earlier method. Table 2 illustrates the results obtained for the methane-heptane binary, utilizing the old and new method, while Table 3 is a summary of the results obtained for the methane-ethane-propane ternary system. It may be seen from inspection of the tables that the two methods of establishing R-K parameters yield *K* values of comparable accuracy, our present method being slightly more accurate than our previous method for the subcritical component. This conclusion must be considered as still tentative, since the two methods have been compared as yet on only a few paraffinic systems. Our earlier procedure has been tested on a great variety of systems containing paraffins from ethane through decane, carbon dioxide, hydrogen sulfide, hydrogen, and nitrogen (*1, 13*). Nevertheless, the new procedure has the advantage, at least in theory, of being self-consistent, since it yields *K* values which converge to unity in a one-component system by virtue of the fact that Equation (5) is satisfied. As may be seen from inspection of Figure 3 of the previous paper (*1*), this result is only approximated with the earlier procedure, small deviations being observed in a certain region. In this respect, the new procedure of fugacity equalization offers an improvement on the earlier one.

NOTATION

a, b = constants in Redlich-Kwong equation, Equation (1)
C_{12} = interaction parameter for pair of components 1 and 2
K = y/x = vapor/liquid equilibrium ratio
P = pressure, vapor pressure
R = gas constant
T = absolute temperature
V = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
ϕ = fugacity coefficient
Ω = dimensionless R-K coefficient

Subscripts

a, b = Redlich-Kwong constant a, b
ij or 12 = binary pair of components i and j or 1 and 2
c = critical state
g, V = gas or vapor phase
l, L = liquid phase

Superscript

s = saturated state

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