0.2. The first peak is dominated by axial convection and the second by Taylor-type diffusion which is a mixture of axial convection and radial diffusoin. The first peak occurs close to $t/\bar{t}$ equal about 0.5 and the second near 1.0

Secondary flows generated by natural convection inhibit the formation of double peaks by reducing radial concentration gradients much more effectively than molecular diffusion can when acting alone; this also reduces the apparent Taylor diffusion coefficient.

Elution curves with double or single peaks observed over the range of conditions studied can be plotted conveniently as reduced dimensionless concentration versus reduced time for a fixed dimensionless distance downstream from the sample injection point. Such plots correlate elution curves whether or not natural convection is significant.

NOTATION

C = solute concentratoin
C_0 = initial solute concentration
D = molecular diffusion coefficient
g = gravitational constant
Gr = Grashof number based on density difference = $8R^3g\Delta\rho/\rho/\nu^2$
k = Taylor dispersion coefficient
L = tube length from injection point to detector
m = mass of solute in sample = $\pi R^2 x_S C_0$
Pe = Peclet number = $2uR/D$
R = tube radius
Re = Reynolds number = $2uR/\nu$
Sc = Schmidt number = ν/D
t = time
$\bar{t}$ = mean residence time L/u
$t/\bar{t}$ = reduced time
u = average fluid velocity
x = axial distance from sample injection point
x_S = slug length
X = dimensionless distance = x/RN_{Pe}
X_S = dimensionless slug length = x_S/RPe
ρ = solvent density
ρ_S = density of injected sample
$\Delta\rho = \rho_S - \rho$ = difference between sample and solvent density
τ = dimensionless time = tD/R^2
ν = kinematic viscosity

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Prediction of the Thermal Conductivity of Gases at High Pressures

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In the past 40 years, a number of investigators have developed several methods to predict the thermal conductivities of gases at high pressure. Comings and Nathan (1947) suggested the use of a plot of thermal conductivity ratio, k/k^* vs. reduced pressure and reduced temperature. Gamson (1949) proposed the first generalized thermal conductivity correlation to make use of the concept of reduced thermal conductivity, k/k_c, where k_c is the critical-thermal conductivity. Unfortunately, the applicability of this correlation is limited to simple fluids where the assumption of the Enskog theory is applicable. Subsequently, Stiel and Thodos (1964), developed a correlation for predicting the thermal conductivity of gases at high pressure completely apart from corresponding states principles. Using a dimensional analysis approach, they related the residual thermal conductivity, $k - k^*$, to the reduced density, ρ_r.

Most recently, Crooks and Daubert (1979) developed a three-

Table 1. Critical Thermal Conductivities of Hydrocarbon Vapors*

Vapor*	Acentric Factor, ω	Crit. Temp. T_c, K	Crit. Pres. P_c, 10^{-5} N/m^2	Crit. Thermal Conductivity k_c, W/m·K
Methane	0.0115	190.6	46.0	0.0312
Ethane	0.0908	305.4	48.8	0.0391
Propane	0.1454	370.0	42.5	0.0433
n-Butane	0.1928	425.2	38.0	0.04777
n-Heptane	0.3506	540.2	27.4	0.0535
Ethene	0.0856	282.4	50.4	0.0379
1-Hexene	0.2848	504.0	31.7	0.0509
1-Heptene	0.358	537.2	28.4	0.0502
1-Octene	0.3858	566.6	26.2	0.0549
Cyclohexane	0.2144	553.4	40.7	0.0533
Benzene	0.2100	562.0	48.9	0.0472
Methylbenzene (Toluene)	0.2566	591.7	41.1	0.0526
Ethylbenzene	0.3011	617.1	36.1	0.0526
1,2-Dimethylbenzene (o-Xylene)	0.3136	630.2	37.3	0.0542
1,3-Dimethylbenzene (m-Xylene)	0.3311	617.0	35.0	0.052
1,4-Dimethylbenzene (p-Xylene)	0.3243	616.2	35.1	0.0528

* Values of ω, T_c, and P_c are taken from Reid et al. (1977).
Values of k_c are calculated by Eq. 1 except for methane and ethane which were found by interpolating experimental values.

parameter corresponding states correlation for predicting the thermal conductivity of nonpolar dense gases. They used heat capacity at constant volume as the third parameter in addition to reduced temperature and reduced pressure for the development of their correlation as it is shown in the following form:

$$\frac{k}{k^*} = \frac{C_v'}{C_v}\left[\left(\frac{k}{k^*}\right)'(T_r,P_r)\right] + \frac{C_v''}{C_v}\left[\left(\frac{k}{k^*}\right)''(T_r,P_r)\right] \qquad (1)$$

where C_v is the constant-volume heat capacity at the temperature and pressure of interest. C_v' and C_v'' are the translational and internal contribution of heat capacity, respectively:

$$C_v = C_v' + C_v'' \qquad (2)$$

Based on the data available on thermal conductivity of gases at high pressure, correlations for calculations of $(k/k^*)'$ and $(k/k^*)''$ were developed, for noncyclic and cyclic hydrocarbon compounds. Accuracy of Crooks' method was much better than Stiel's method and therefore it was recommended by the American Petroleum Institute (1977) as the best method available for predicting the thermal conductivity of dense gases.

The main objective of this work was to develop a Pitzer-type generalized correlation to predict thermal conductivity of gases at high pressures with fewer input parameters than current methods.

TECHNICAL DEVELOPMENTS OF THE PROPOSED GENERALIZED THREE-PARAMETER CORRESPONDING STATES CORRELATION

To use the corresponding states technique for prediction of thermal conductivity of complex gases a third parameter, beside the reduced temperature and pressure is needed. Although several shape factors have been introduced, the Pitzer acentric factor has been the most successful parameter capable of characterizing complex molecules. The Pitzer three-parameter corresponding states (Pitzer et al., 1955) suggests that the compressibility, Z, of a fluid can be related to the compressibility of a simple fluid $Z^{(0)}$ and an acentric fluid $Z^{(1)}$ as follows:

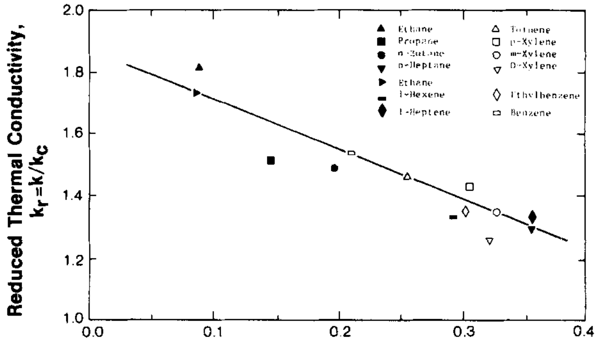

Figure 1. Reduced thermal conductivity versus acentric factor at $T_r = 1.05$ and $P_r = 2.0$.

$$Z = Z^{(0)} + \omega Z^{(1)} \qquad (3)$$

where ω is the acentric factor of the fluid. $Z^{(0)}$ and $Z^{(1)}$ are functions of T_r and P_r. Application of Eq. 3 for the reduced thermal conductivity, k/k_c suggests that:

$$k_r = \frac{k}{k_c} = k_r^{(0)} + \omega k_r^{(1)} \qquad (4)$$

where $k_r^{(0)}$ is the reduced thermal conductivity of simple fluid (ω = 0, as inert gases) and $k_r^{(1)}$ is a complicated function. In using Eq.

Table 2. Effect of Pressure on Vapor Thermal Conductivity, Simple Fluid Term, $k_r^{(1)}$

Reduced Temp. T_r	Reduced Pressure, P_r 0.2	0.5	1.0	1.5	2.0	3.0	4.0	6.0	8.0	10.0
1.00	1.1880	1.3307	2.0000	4.1517	4.4282	4.7900	5.2140	5.7989	6.2080	6.5132
1.05	1.3002	1.3640	1.8922	3.2806	3.7990	4.4915	4.7590	5.2817	5.7710	6.2040
1.10	1.4300	1.4810	1.8660	2.5989	3.3334	4.1068	4.4746	4.9502	5.374	5.8812
1.15	1.5182	1.5365	1.8356	2.2978	2.9769	3.8583	4.4676	4.9404	5.3734	5.8760
1.20	1.8311	1.8956	2.1200	2.3983	2.8809	3.5626	4.2067	4.9285	5.3731	5.8699
1.40	2.1838	2.2520	2.3589	2.5291	2.7120	3.3000	4.0020	4.6327	5.2404	5.7656
1.60	2.5971	2.6589	2.7305	2.8572	3.0035	3.3760	3.8239	4.4385	4.8967	5.3031
2.00	3.6763	3.6984	3.7418	3.9161	3.9594	4.137	4.3768	4.7138	5.0462	5.3614
3.00	6.9896	7.0010	7.0310	7.0617	7.1079	7.1452	7.2197	7.4077	7.5915	7.7685

TABLE 3. EFFECT OF PRESSURE ON VAPOR THERMAL CONDUCTIVITY, CORRECTION TERM, $k_r^{(2)}$

Reduced Temp. T_r	Reduced Pressure, P_r 0.2	0.5	1.0	1.5	2.0	3.0	4.0	6.0	8.0	10.0
1.00	1.6900	1.6990	2.0000	2.0619	2.3112	2.3140	2.3160	2.3180	2.3210	2.3212
1.05	1.7200	1.7290	1.8100	1.8170	2.1318	2.1912	2.3010	2.3380	2.3398	2.3400
1.10	1.8001	1.8211	1.8300	1.8310	1.9672	2.1334	2.1369	2.3614	2.3988	2.4105
1.15	2.0599	2.0601	2.0661	2.0700	2.0801	2.1269	2.2246	2.3780	2.4618	2.4622
1.20	2.1441	2.1539	2.1629	2.1681	2.1689	2.1901	2.2319	2.3981	2.4640	2.4701
1.40	2.6496	2.6772	2.6865	2.6889	2.6900	2.6911	2.7001	2.7119	2.8079	2.8810
1.60	3.2184	3.2448	3.2559	3.2886	3.3142	3.3292	3.3343	3.3352	3.3869	3.4525
2.00	4.5222	4.5330	4.5465	4.6871	4.6378	4.7108	4.8148	4.8119	4.8850	4.9885
3.00	8.4002	8.4158	8.4234	8.4503	8.4504	8.5038	8.6083	8.6204	8.6732	8.7454

4, two facts must be kept in mind: that the critical thermal conductivity of many substances is not known, and $k_r^{(0)}$ and $k_r^{(1)}$ must be determined as functions of reduced temperature and pressure. Consequently, a bank of data on thermal conductivity of 16 hydrocarbons listed in Table 1 was prepared (Crooks and Daubert, 1979). The critical thermal conductivity, k_c, was determined for each compound by interpolation of experimental data or by using Eq. 1 at $T = T_c$ and $P = P_c$. Values of k_c for 16 hydrocarbons used in this work are also given in Table 1.

In order to show that the acentric factor is capable of correlating the reduced thermal conductivity, at $T_r = 1.05$ and $P_r = 2$ where experimental data were available for 13 hydrocarbons, k_r for each compound was determined. A plot of k_r vs. ω is shown in Figure 1. It is obvious that at a given T_r and P_r, the relationship between k_r and ω is almost linear. Since the data available are for hydrocarbons having acentric factors in the range of 0.09–0.358, k_r at $\omega = 0$ and $\omega = 0.5$ can be determined from the plot of k_r vs. ω. The following linear relation between k_r and ω, when ω ranges from 0 to 0.5, is proposed.

$$k_r = (0.5 - \omega)k_r^{(1)} + \omega k_r^{(2)} \tag{5}$$

where

$$k_r^{(1)} = 2k_r \text{ (at } \omega = 0.0\text{)}$$

$$k_r^{(2)} = 2k_r \text{ (at } \omega = 0.5\text{)}$$

At each T_r and P_r, a plot similar to Figure 1 can be prepared, and from the intercepts of the line with the k_r axis at $\omega = 0$ and $\omega = 0.5$, values of $k_r^{(1)}$ and $k_r^{(2)}$ can be determined. Since complete data for all the hydrocarbons listed in Table 1 were not available, compounds; ethane, 1-heptene, and benzene were chosen as the reference compounds. At every T_r and P_r, values of $k_r^{(1)}$ and $k_r^{(2)}$ with respect to the reference compounds were determined and they are listed in Tables 2 and 3. Graphical representation of these Tables are shown in Figures 2 and 3.

Experimental thermal conductivity data for 16 compounds listed in Table 1 were used for the evaluation of the proposed correlation. For each compound reduced thermal conductivity at T_r and P_r which values of $k_r^{(1)}$ and $k_r^{(2)}$ are given in Tables 2 and 3 was determined through interpolation of experimental values and then thermal conductivity was determined as follows:

$$k = k_c k_r \tag{6}$$

A summary of results is shown in Table 4. Average deviation of 5% was observed for 608 data points. It is quite obvious that some part of the errors involved in these predictions is due to the accuracy of values of k_c listed in Table 1. Equation 5 can also be used for prediction of thermal conductivity if at least at one point the thermal conductivity is known:

$$k_2 = k_1 \frac{k_{r_1}}{k_{r_2}} \tag{7}$$

$k_r^{(1)}$ and $k_r^{(2)}$ can be determined from Tables 2 and 3 or from Figures 2 and 3 and since k_1 (at some temperature and pressure) is known, k_2 (at the temperature and pressure of interest) can be calculated. In this manner, less error will be observed. However, the accuracy of the proposed correlation is about the accuracy of experimental values for thermal conductivity of dense gases at high pressures. Average deviations for predicting thermal conductivity from Eq. 1 (Crooks and Daubert's method) was about 4.5%.

Although the accuracy of the proposed correlation is a little less than the accuracy of Eq. 1, it is in more general form and it is much

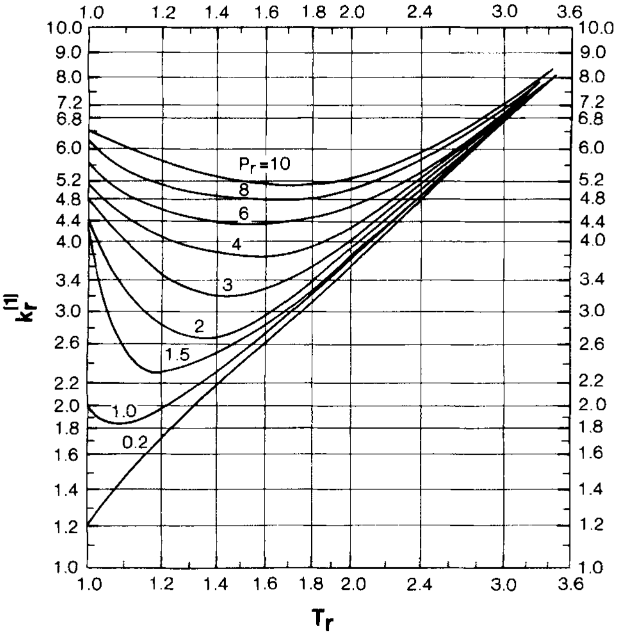

Figure 2. Generalized chart for $k_r^{(1)}$.

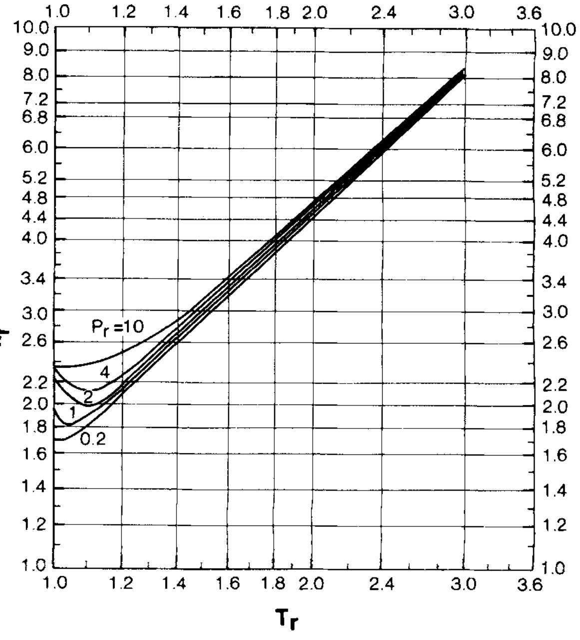

Figure 3. Generalized chart for $k_r^{(2)}$.

TABLE 4. EVALUATION OF THE PROPOSED CORRELATION FOR THE PREDICTION OF THERMAL CONDUCTIVITY OF PURE COMPONENT VAPORS

Compound	Number of Points Evaluated	Reduced Temp. Range	Reduced Pres. Range	Thermal Conductivity Range, W/m·K*	Deviations, %**	
					Avg.	Max.
Methane	35	1.20–3.00	0.2–10.0	0.032–0.104	8.8	28.9
Ethane	90	1.00–3.00	0.2–10.0	0.022–0.094	3.1	10.0
Propane	54	1.00–1.20	0.5–10.0	0.031–0.097	10.4	19.0
n-Butane	24	1.00–1.05	0.2–6.0	0.035–0.104	4.2	8.0
n-Heptane	18	1.00–1.10	1.5–8.0	0.069–0.095	3.0	3.9
Ethene	30	1.00–1.20	1.0–6.0	0.026–0.097	3.5	10.1
1-Hexene	54	1.00–1.40	0.5–10.0	0.035–0.090	4.1	10.0
1-Heptene	90	1.00–3.00	0.2–10.0	0.042–0.095	3.1	11.6
1-Octene	5	1.00–1.00	2.0–8.0	0.073–0.083	5.9	9.2
Cyclohexane	18	1.05–1.15	1.5–8.00	0.048–1.02	11.2	16.0
Benzene	30	1.00–1.20	1.5–8.0	0.057–0.092	8.1	16.0
Methylbenzene (Toluene)	24	1.00–1.15	1.0–6.0	0.052–0.093	5.1	12.0
Ethylbenzene	27	1.00–1.10	1.5–10.0	0.062–0.095	3.5	6.0
1,2-Dimethylbenzene (o-Xylene)	32	1.00–1.15	1.0–10.0	0.059–0.093	5.2	10.8
1,3-Dimethylbenzene (m-Xylene)	32	1.00–1.15	1.0–10.0	0.061–0.093	3.2	10.0
1,4-Dimethylbenzene (p-Xylene)	45	1.00–1.20	0.5–10.0	0.045–0.097	3.8	15.2
	608	1.00–3.00	0.2–10.0	0.022–0.104	5.0	28.9

* Experimental values of thermal conductivity from Crooks and Daubert (1979).

** $\% \text{ deviation} = E = \frac{\text{predicted value-experimental value}}{\text{experimental value}} \times 100$

$\text{Average deviation} = \frac{1}{n}\sum|E|$

n = number of data points

simpler to use. In the proposed correlation, critical temperature and pressure, critical thermal conductivity, and the acentric factor of the substance must be known in order to predict its thermal conductivity at any temperature and pressure. If critical thermal conductivity is not known, then at least thermal conductivity at one temperature and pressure must be known for prediction at other temperatures and pressures. For computer uses, appropriate analytical correlations based on the data in Tables 2 and 3 can be developed for $k_r^{(1)}$ and $k_r^{(2)}$ as functions of T_r and P_r.

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NOTATION

C_v = constant-volume heat capacity
C_v' = translational contribution of C_v
C_v'' = internal contribution of C_v
k = thermal conductivity
k_c = critical thermal conductivity
k_r = reduced thermal conductivity
k^* = thermal conductivity at low pressure
$k_r^{(1)}, k_r^{(2)}$ = reduced thermal conductivity of simple and acentric fluids defined in Eq. 5
k_{rl} = reduced thermal conductivity at T_{rl} and P_{rl}
$(k/k^*)'$ = translational contribution of (k/k^*)
$(k/k^*)''$ = internal contribution of (k/k^*)
P = pressure
P_c = critical pressure
P_r = reduced pressure
T = temperature
T_c = critical temperature
T_r = reduced temperature
Z = compressibility factor
Z_c = critical compressibility
Z_r = reduced compressibility
ρ_r = reduced density
ω = acentric factor

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