

Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworths: London, 1982; Chapter 1.
 Scott, R. L.; van Konynenburg, P. H. *Discuss. Faraday Soc.* 1970, 49, 87.
 Shukla, K. P. *Molec. Phys.* 1987, 62, 1143.
 Shukla, K. P.; Haile, J. M. *Molec. Phys.* 1987, 62, 617.

van Konynenburg, P. H.; Scott, R. L. *Phil. Trans.* 1980, A298, 495.
 Weeks, J. D.; Chandler, D.; Andersen, H. C. *J. Chem. Phys.* 1971a, 54, 5237; *Phys. Rev.* 1971b, A4, 1597.

Received for review July 17, 1987

Accepted December 7, 1987

Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties

Ting-Horng Chung,[†] Mohammad Ajlan,[‡] Lloyd L. Lee,* and Kenneth E. Starling

School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma 73019

Correlations are presented for the viscosity and thermal conductivity of nonpolar, polar, and associating fluids over the wide ranges of *PVT* states. Empirically correlated density-dependent functions were developed to extend the kinetic gas theory to include dense fluids. Extensive comparisons with experimental data of pure fluids are made. The average absolute deviation is 4% for viscosity predictions and 6% for thermal conductivity predictions. The conformal solution model mixing rules have shown to yield predictions of viscosity and thermal conductivity for nonassociating mixtures of sufficient accuracy for most industrial uses. The viscosity and thermal conductivity predictive procedure is simple and straightforward. It requires only critical constants and acentric factors for nonpolar fluids. For polar and associating fluids, the dipole moment and an empirically determined association parameter, in addition, are required.

Transport properties are important quantities required in engineering design for production, transportation, and processing. For example, viscosity is an important parameter for the determination of pipeline size and the power required to pump fluids through it. Viscosity also enters into heat-exchanger and separation equipment sizing and is a critical parameter for the recovery efficiency of reservoir oils. However, our understanding of the transport properties is far behind that of equilibrium properties. The difficulties we face in the study of transport properties are twofold: one is the inherent difficulties involved in accurate measurements, and the other is the complexity involved in theoretical treatments. Applications of theoretical developments in either the distribution function approach—a generalized Boltzmann equation method (Chapman and Cowling, 1952)—or the time-correlation function approach (Zwanzig, 1965; Steele and Hanley, 1969) have only been possible for simple cases such as dilute gases of simple molecules. For dense gas properties, one of the very few theoretical results is the Enskog dense gas theory for the hard-sphere-potential model (Chapman and Cowling, 1952). Following this theory, many investigators have proposed correlations for the viscosity ratio (η/η_0) as a function of reduced density and reduced temperature (Reid et al., 1977).

Most of the available methods for the prediction of transport properties are empirical correlations and are limited to specified state regions and fluids. A good review of these methods was given by Reid et al. (1977). They concluded that none of the methods available are particularly reliable, especially for polar fluids. Methods based on the principle of corresponding states (Helfand and Rice, 1960; Gubbins, 1973) have been widely used for the determination of the transport properties of simple dense fluids. For simple liquids (Ar, Kr, Xe, and CH₄), the

principle has been shown to be accurately obeyed (Tham and Gubbins, 1969). A conformal solution theory has also been developed (Mo and Gubbins, 1976) for mixtures of such simple fluids. For more complicated molecules, the liquid viscosity has been shown not to obey the simple corresponding states principle (Tham and Gubbins, 1970). The discrepancy is more obvious for thermal conductivity since polyatomic fluids do not obey the principle even at dilute gas conditions (Chung et al., 1984b). This is because the corresponding states arguments do not correctly take into account the effect of internal degrees of freedom on the thermal conductivity (Hanley, 1977). Recently, the applicability of corresponding states for thermodynamic properties has been broadened considerably by the introduction of state-dependent shape factors (Leland et al., 1968; Rowlinson and Watson, 1969) to include substances of more complicated molecules (Haile et al., 1976; Ely and Hanley, 1981, 1983). Unfortunately, this method is currently applicable to nonpolar fluids only, and its use requires complicated procedures.

The methods presented in this work for the prediction of transport properties are relatively simple and can be applied to both polar and associating fluids. The viscosity and thermal conductivity of dense fluids are empirically correlated as functions of density and temperature. For mixtures, the predictive method is similar in essence to the conformal-solution model. Based on this model, mixing rules are developed for all parameters; the viscosity and thermal conductivity correlations are the same as those for pure fluids.

The correlation of low-pressure gas viscosity and thermal conductivity based on the kinetic gas theory has been published earlier (Chung et al., 1984b), where accurate models were presented for dilute gas viscosity and thermal conductivity of nonpolar, polar, and associating fluids. The low-pressure gas viscosity and thermal conductivity models are now extended to fluids at high densities by introducing empirically correlated, density-dependent functions. As fluid density approaches zero, these correlations will reduce to the low-pressure gas expressions. These correlations use

[†]Current address: National Institute for Petroleum and Energy Research (NIPER), Bartlesville, OK 74003.

[‡]Current address: Department of Chemical Engineering, University of Petroleum and Minerals, Dhahran, Saudi Arabia.

Pitzer's acentric factor (ω), the dimensionless dipole moment (μ_r), and an empirically determined association parameter (κ) to characterize the molecular structure effect of polyatomic molecules, the polar effect, and the hydrogen-bonding effect, respectively. This work provides a means to predict the viscosity and thermal conductivity for polar fluids with straightforward calculations.

The conformal-solution-model mixing rules have been shown to yield predictions with reasonable accuracy for all mixtures except highly polar mixtures. Over 40 low-pressure gas systems and 80 dense gas and liquid systems have been tested. The results were found to be of reasonable accuracy suitable for most engineering design purposes.

Development of Correlations

(A) **Dilute Gas Viscosity and Thermal Conductivity.** The Chapman-Enskog theory (Chapman and Cowling, 1952) for the dilute gas viscosity is written as

$$\eta_0 = (26.69 \times 10^{-6}) \frac{(MT)^{1/2}}{\sigma^2 \Omega^*} \quad (1)$$

where η_0 = viscosity, P; M = molecular weight, g/mol; T = temperature, K; σ = potential distance parameter, Å; and Ω^* = the reduced collision integral which depends upon the intermolecular potential chosen. Neufeld et al. (1972) proposed an empirical equation which is convenient for computer application,

$$\Omega^* = \left(\frac{A}{T^{*B}} \right) + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{GT^{*B} \sin(ST^{*W} - H)} \quad (2)$$

where $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, $F = 2.43787$, $G = -6.435 \times 10^{-4}$, $H = 7.27371$, $S = 18.0323$, and $W = -0.76830$. The dimensionless temperature T^* is related to the potential energy parameter (ϵ) and Boltzmann's constant (k) by

$$T^* = kT/\epsilon \quad (3)$$

Rigorously, eq 1 with eq 2 is only applicable for simple molecular gases such as argon and methane. To extend to polyatomic molecular gases (polar and nonpolar), eq 1 is multiplied by a factor F_c to account for molecular structure and polar effects. The following relations are also employed in conjunction with eq 1:

$$\sigma = 0.809 V_c^{1/3} \quad (4)$$

$$\epsilon/k = T_c/1.2593 \quad (5)$$

where ϵ/k and the critical temperature (T_c) are in K, σ in Å, and the critical volume (V_c) in cm³/mol. Thus, eq 1, 4, and 5 after simplification and multiplication by F_c result in

$$\eta_0 = (4.0785 \times 10^{-5}) \frac{(MT)^{1/2}}{V_c^{2/3} \Omega^*} F_c \quad (6)$$

The factor F_c has been empirically found to be

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \quad (7)$$

where ω is the acentric factor and κ is a correction factor for hydrogen-bonding effect of associating substances such as alcohols, acids, and water. The value of κ which could be determined empirically by fitting the dilute gas viscosity data of associating substances will be employed later in this paper as an additional characterization parameter for associating fluids for the correlations of viscosity and

Table I. Association Parameters

compd	κ	compd	κ
methanol	0.215175	1-pentanol	0.121555
ethanol	0.174823	1-hexanol	0.114230
1-propanol	0.143453	1-heptanol	0.108674
2-propanol	0.143453	acetic acid	0.091549
1-butanol	0.131671	water	0.075908
2-methyl-1-propanol	0.131671		

thermal conductivity. The κ values of some alcohols and water are given in Table I. The term μ_r is a dimensionless dipole moment, when V_c is in cm³/mol, T_c in K, and μ in D,

$$\mu_r = 131.3\mu/(V_c T_c)^{1/2} \quad (8)$$

Extensive information on the μ values was provided by Reid et al. (1977). For nonpolar gases, only the two first terms in eq 7 are used since the other two terms become zero.

The thermal conductivity for dilute gases is written as

$$\lambda_0 = 7.452(\eta_0/M)\Psi \quad (9)$$

where λ_0 = dilute gas thermal conductivity, cal/(cm·s·K); η_0 = dilute gas viscosity, P; $\Psi = 1 + \alpha\{[0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z]/[0.6366 + \beta Z + 1.061\alpha\beta]\}$; $\alpha = (C_v/R) - (3/2)$; $\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$; $Z = 2.0 + 10.5T_c^{-1}$; C_v = ideal gas heat capacity at constant volume, cal/(mol·K); and R = gas constant, 1.987 cal/(mol·K). The term β which theoretically equals $\eta/\rho D$ is empirically correlated as a function of acentric factor for nonpolar substances. For polar substances, β values for some compounds were given previously (Chung et al., 1984b). The ideal gas heat capacity (C_v) can be obtained from published correlations (Passut and Danner, 1972; Aly and Lee, 1981; Fakeeha et al., 1983).

Extensive comparisons of eq 6 and 9 with experimental data show that the average absolute deviation (AAD) of the predicted pure dilute gas properties with published data is 1.5% for viscosity and 2.0% for thermal conductivity (Chung et al., 1984b). These correlations can be applied to wide classes of substances including polar, nonpolar, and hydrogen-bonding compounds.

(B) **Viscosity for Dense Fluids.** For dense fluids, eq 6 is extended to account for the effects of temperature and pressure by developing an empirically correlated function of density and temperature, as shown below:

$$\eta = \eta_\kappa + \eta_p \quad (\text{in P}) \quad (10)$$

where $\eta_\kappa = \eta_0[1/G_2 + A_6 Y]$; $\eta_p = [36.344 \times 10^{-6} \cdot (MT_c)^{1/2}/V_c^{2/3}]A_7 Y^2 G_2 \exp(A_8 + A_9/T^* + A_{10}/T^{*2})$; $Y = \rho V_c/6$; $G_1 = (1.0 - 0.5Y)/(1 - Y)^3$; and $G_2 = \{A_1[1 - \exp(-A_4 Y)]/Y + A_2 G_1 \exp(A_5 Y) + A_3 G_1\}/(A_1 A_4 + A_2 + A_3)$. η_0 is the viscosity of low-pressure gas given by eq 6, and the constants A_1 – A_{10} are linear functions of the acentric factor (ω), the reduced dipole moment (μ_r), and the association factor (κ), fitted as follows:

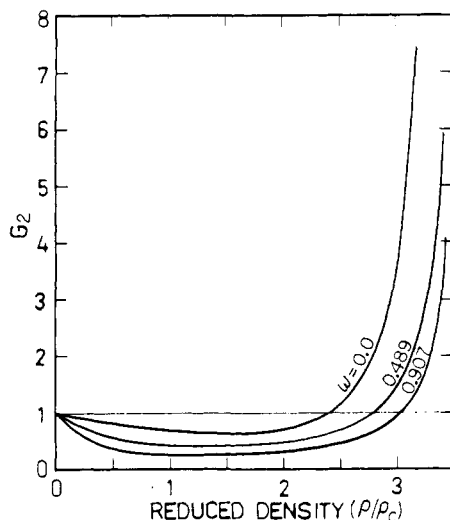
$$A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_r^4 + a_3(i)\kappa \quad i = 1, 10 \quad (11)$$

where a_0 , a_1 , a_2 , and a_3 are given in Table II. Constants a_0 and a_1 were determined by regression of the viscosity data for nonpolar fluids, and a_2 and a_3 were determined similarly from the data of polar and associating fluids. For nonpolar substances, only the first two terms are taken into account. The third term is included for polar substances and the last term for hydrogen-bonding substances.

The behavior of G_2 as a function of reduced density is shown in Figure 1. G_2 is seen to approach unity as density approaches zero, and it sharply increases with density at higher density values. Thus, at the limiting value of low

Table II. Constants Used for the Generalized Viscosity Correlation

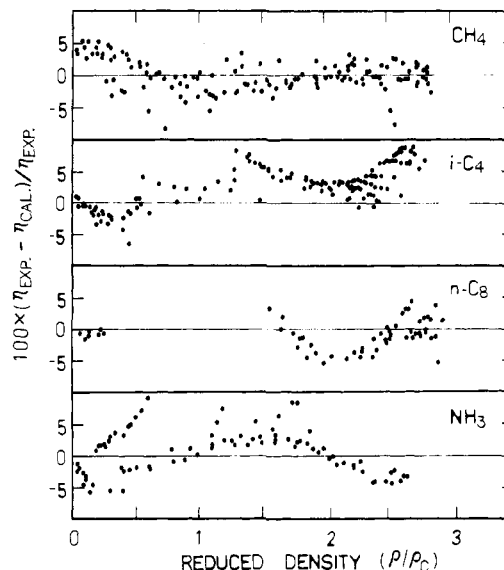
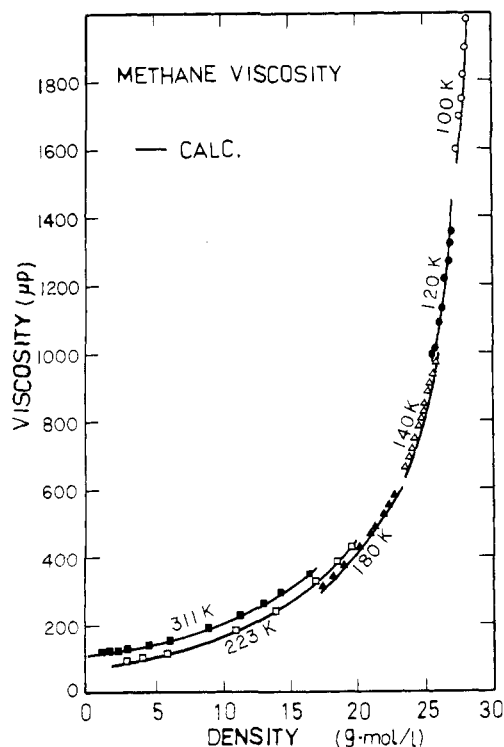
<i>i</i>	$a_0(i)$	$a_1(i)$	$a_2(i)$	$a_3(i)$
1	6.324 02	50.411 90	-51.680 10	1189.020 00
2	0.121 02 × 10 ⁻²	-0.115 36 × 10 ⁻²	-0.625 71 × 10 ⁻²	0.372 83 × 10 ⁻¹
3	5.283 46	254.209 00	-168.481 00	3898.270 00
4	6.622 63	38.095 70	-8.464 14	31.417 80
5	19.745 40	7.630 34	-14.354 40	31.526 70
6	-1.899 92	-12.536 70	4.985 29	-18.150 70
7	24.274 50	3.449 45	-11.291 30	69.346 60
8	0.797 16	1.117 64	0.123 48 × 10 ⁻¹	-4.116 61
9	-0.238 16	0.676 95 × 10 ⁻¹	-0.816 30	4.025 28
10	0.686 29 × 10 ⁻¹	0.347 93	0.592 56	-0.726 63

**Figure 1.** G_2 values as function of density.

density, the η_p term is negligible and eq 10 reduces to eq 6. On the other hand, at extremely high density, η_k is small and η_p is the major contributing term. This feature is significant in allowing eq 10 to describe viscosity over the entire PVT region.

Equation 10 has been tested for pressures up to 3447 bar and temperatures from 70 to 973 K. Table III summarizes the predicted results for the viscosity of 37 substances and provides data source information. Most viscosity values are predicted within about 3% deviation for paraffins and olefins, whereas the deviations are slightly higher for ring compounds with an average absolute deviation (AAD) of 4%. Equation 10 also gave satisfactory results for non-hydrocarbons, polar, and hydrogen-bonding compounds. The deviations of eq 10 from experimental values for some substances are shown in Figure 2. The comparison of the predicted viscosity (line) with the experimental data (symbols) is shown in Figure 3 for methane from the dilute gas state to the dense liquid. The viscosity-density plot shows that the viscosity increases drastically with density as the fluid becomes dense, which indicates that, for prediction of dense fluid viscosity, density is a very sensitive parameter. For this reason, the high accuracy region for the correlation generally corresponds to reduced temperatures (T/T_c) greater than about 0.4 and reduced densities (ρ/ρ_c) below about 2.5, although the correlation yields reasonable results somewhat beyond this region.

(C) Thermal Conductivity for Dense Fluids. The same approach was employed to develop the thermal conductivities of pure fluids at high pressures (or densities) as for viscosity. The low-pressure-gas thermal conduc-

**Figure 2.** Comparison of calculated and experimental viscosity.**Figure 3.** Comparison of calculated and experimental viscosity of methane.

tivity, eq 9, was modified by introducing an empirically correlated function,

$$\lambda = \lambda_k + \lambda_p \quad (12)$$

where $\lambda_k = \lambda_0[(1/H_2) + B_6 Y]$; $\lambda_p = [3.039 \times 10^{-4}(T_c/M)^{1/2}/V_c^{2/3}]B_7 Y^2 H_2 T_r^{1/2}$; λ = thermal conductivity, cal/(cm·s·K); λ_0 = low-pressure-gas thermal conductivity, eq 9; T_r = reduced temperature, T/T_c ; and $H_2 = \{B_1[1 - \exp(-B_4 Y)]/Y + B_2 G_1 \exp(B_5 Y) + B_3 G_1\}/(B_1 B_4 + B_2 + B_3)$. The constants B_1 – B_7 are functions of the acentric factor (ω), the reduced dipole moment (μ_r) (as defined in eq 8), and the association factor (κ) as shown below:

$$B_i = b_0(i) + b_1(i)\omega + b_2(i)\mu_r^4 + b_3(i)\kappa \quad i = 1, 7 \quad (13)$$

with b_0 , b_1 , b_2 , and b_3 given in Table IV obtained from the regression analysis of thermal conductivity data for polar, nonpolar, and associating fluids.

Table III. Comparisons of Calculated and Experimental Viscosities for Pure Fluids

fluid	data no.	temp range, K	pressure range, bar	deviation, %		ref ^a
				AAD	max	
methane	466	91-511	1-680	2.40	-8.42	1,2,3,4,5,6,7,8,39, ^b 40 ^b
ethane	60	311-444	4-544	1.90	-4.84	9,10, ^a 41 ^b
propane	136	173-411	7-544	2.18	8.67	2,9,39, ^b 40, ^b 41 ^b
<i>n</i> -butane	70	213-444	7-544	2.13	-9.67	9,10,11,40 ^b
<i>n</i> -pentane	85	173-470	1-204	2.57	-11.45	10,12,40 ^b
<i>n</i> -hexane	249	193-548	1-500	2.42	11.64	10,13,40 ^b
<i>n</i> -heptane	268	263-548	1-500	2.17	13.37	10,14,40 ^b
<i>n</i> -octane	232	283-569	1-500	2.12	-12.97	10,13,40 ^b
<i>n</i> -nonane	17	263-423	1	4.41	-7.42	10,14,40 ^b
<i>n</i> -decane	48	253-444	1-476	2.91	-9.92	10,15,40 ^b
<i>n</i> -undecane	23	263-474	1	7.11	-12.56	10,14
<i>n</i> -dodecane	41	273-408	1-3447	7.29	-16.92	10,13,16,40 ^b
<i>n</i> -tridecane	21	273-474	1	4.19	16.00	10,14,42 ^b
<i>n</i> -tetradecane	10	283-373	1	5.12	13.86	10,42 ^b
<i>n</i> -pentadecane	29	293-408	1-3447	4.68	-16.80	10,16
<i>n</i> -hexadecane	69	293-523	1-2731	3.91	-15.69	10,17,18,42 ^b
<i>n</i> -heptadecane	18	303-573	1	5.12	15.45	10,14 ^b
<i>n</i> -octadecane	24	303-408	1-1724	4.10	-10.28	10,16
<i>n</i> -eicosane	12	313-493	1	2.56	-4.84	10
isobutane	524	273-548	1-686	4.04	11.43	19,21,40 ^b
isopentane	260	273-573	0-588	6.07	20.15	20,22,23,24,25,26,40 ^b
ethylene	38	298-773	1-810	1.94	-6.72	10,22, ^b 40 ^b
propylene	74	373-573	1-810	1.75	7.33	10,28,40 ^b
benzene	35	290-700	1-6.6	4.92	11.82	10,40, ^b 43 ^b
toluene	16	273-873	1	7.38	-13.05	10,40, ^b 43 ^b
oxygen	232	69-300	0.1-346	2.33	8.02	29,30,31,32,8,40 ^b
nitrogen	124	183-373	1-257	1.24	-3.81	33,34,35,36,40 ^b
fluorine	194	70-300	1-221	4.12	12.04	37,40 ^b
carbon monoxide	38	70-348	1	5.25	13.89	5,8,40 ^b
carbon dioxide	37	297-475	1-68	1.96	-9.59	27,40 ^b
ammonia	212	298-523	4.6-200	3.42	13.20	10,38,40 ^b
monochlorodifluoromethane	118	193-473	0.3-30	5.69	19.01	10
ethyl ether	12	273-873	1	1.91	5.29	10
acetic acid	3	303-323	1	0.60	0.95	10
methanol	23	273-503	sat.	3.00	7.48	10,40 ^b
1-propanol	22	293-473	sat.	6.08	12.47	10,40 ^b
water	407	273-973	1-800	3.08	-14.69	10

^a Data references: (1) Lee (1965), (2) Huang et al. (1966), (3) Haynes (1973), (4) Kestin and Leidenfrost (1959), (5) Barua et al. (1964), (6) Diller (1980), (7) Gonzalez et al. (1966), (8) Boon et al. (1967), (9) Starling (1962), (10) Vargaftik (1975), (11) Lipkin et al. (1942), (12) Lee and Ellington (1965a), (13) Dymond and Young (1980), (14) Doolittle and Peterson (1951), (15) Lee and Ellington (1965b), (16) Dixon (1959), (17) Nederbragt and Boelhouwer (1947), (18) Dymond et al. (1980), (19) Agaev and Yusibova (1969), (20) Yusibova and Agaev (1969), (21) Gonzalez and Lee (1966), (22) Golubev (1959), (23) Rappenecher (1910), (24) Day (1932), (25) McCoubrey and Singh (1963), (26) Bleakney (1932), (27) Kestin and Whitelaw (1963), (28) Hongo (1979), (29) Haynes (1977), (30) Saji and Kobayashi (1964), (31) Van Itterbeek and Van Paemel (1941), (32) Kestin and Leidenfrost (1969), (33) Flynn et al. (1963), (34) Gracki et al. (1969), (35) Goldman (1963), (36) Kestin et al. (1971), (37) Haynes (1974), (38) Iwasaki and Takahashi (1968), (39) Giddings et al. (1966), (40) Stephan and Lucas (1979), (41) Diller (1981), (42) Rastorguev and Keramidi (1974), (43) Medani and Hasan (1977). ^b Data sources not included in the calculation.

Table IV. Constants Used for the Generalized Correlation for Thermal Conductivity

<i>i</i>	$b_0(i)$	$b_1(i)$	$b_2(i)$	$b_3(i)$
1	2.416 57	0.748 24	-0.918 58	121.721 00
2	-0.509 24	-1.509 36	-49.991 20	69.983 40
3	6.610 69	5.620 73	64.759 90	27.038 90
4	14.542 50	-8.913 87	-5.637 94	74.343 50
5	0.792 74	0.820 19	-0.693 69	6.317 34
6	-5.863 40	12.800 50	9.589 26	-65.529 20
7	81.171 00	114.158 00	-60.841 00	466.775 00

The behavior of the H_2 function is quite similar to the G_2 function for viscosity as shown in Figure 1. H_2 approaches unity as density approaches zero, and thus eq 12 is reduced to eq 9 for the low-pressure-gas thermal conductivity. At higher densities, the H_2 function increases steeply with density, causing the second term, λ_p , to become dominant. Thus, by use of this density-dependent function (H_2), eq 12 covers all PVT states.

The accuracies of thermal conductivity predictions are summarized in Table V. The average absolute deviations (AAD) between the calculated and experimental values range between 1.9% and 5.1% for paraffins and 6.0% and 8.6% for aromatics. For polar and associating compounds such as chloroform, ammonia, and alcohols, the discrep-

ancies vary between 3.3% and 8.3% AAD. Some non-hydrocarbons such as nitrogen, oxygen, CO₂, and SO₂ are also included in Table V. It should be noted here that the data in Table V are all outside the critical region where the thermal conductivity generally shows a hump (Ely and Hanley, 1983). The deviation in the predictions depends upon the source of data. Due to the inherent difficulties involved in the measurement of thermal conductivity, it is quite common to have large discrepancies (5-15%) between data of different sources for the same fluid. The deviations of eq 12 from experimental values for some substances are shown in Figure 4.

(D) Mixing Rules for Mixture Properties. The conformal-solution model was utilized for the prediction of viscosity and thermal conductivity of mixtures. The theoretical basis of these mixing rules is the conformal-solution theory of Mo and Gubbins (1976). According to their model, the properties of mixtures are calculated from the same correlations (eq 10 and 12) as for a pure fluid, except that the characterization parameters, σ , ϵ , M , ω , μ , and κ are replaced by σ_m , ϵ_m , M_m , ω_m , μ_m , and κ_m , respectively, which are functions of composition and parameters of pure components. The following mixing rules for σ_m , ϵ_m , and ω_m are compatible with the three-parameter cor-

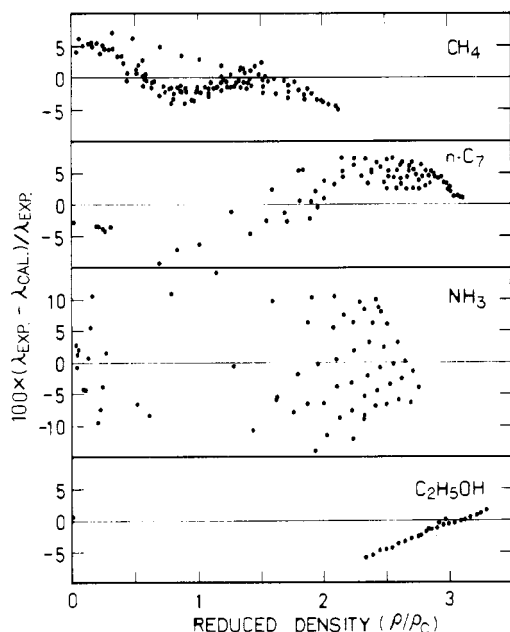


Figure 4. Comparison of calculated and experimental thermal conductivity.

responding states theory for thermodynamic properties (Lee et al., 1977) and yield reasonably accurate predictions of viscosity and thermal conductivity for mixtures,

$$\sigma_m^3 = \sum_i \sum_j X_i X_j \sigma_{ij}^3 \quad (14)$$

$$\epsilon_m/k = [\sum_i \sum_j X_i X_j (\epsilon_{ij}/k) \sigma_{ij}^3] / \sigma_m^3 \quad (15)$$

$$V_{cm} = (\sigma_m/0.809)^3 \quad (16)$$

$$T_{cm} = 1.2593 \epsilon_m/k \quad (17)$$

$$\omega_m = [\sum_i \sum_j X_i X_j \omega_{ij} \sigma_{ij}^3] / \sigma_m^3 \quad (18)$$

$$M_m = \{[\sum_i \sum_j X_i X_j (\epsilon_{ij}/k) \sigma_{ij}^2 M_{ij}^{1/2}] / [(\epsilon_m/k) \sigma_m^2]\}^2 \quad (19)$$

$$\mu_m^4 = \{\sum_i \sum_j X_i X_j (\mu_i^2 \mu_j^2) / [(\epsilon_{ij}/k) \sigma_{ij}^3]\} \sigma_m^3 (\epsilon_m/k) \quad (20)$$

$$\kappa_m = \sum_i \sum_j X_i X_j \kappa_{ij} \quad (21)$$

$$\mu_{rm} = 131.3 \mu_m / (V_{cm} T_{cm})^{1/2} \quad (22)$$

where the binary parameters are given by the combining rules,

$$\sigma_{ij} = \xi_{ij} (\sigma_i \sigma_j)^{1/2} \quad (23)$$

$$\epsilon_{ij}/k = \zeta_{ij} [(\epsilon_i/k)(\epsilon_j/k)]^{1/2} \quad (24)$$

$$\omega_{ij} = 1/2 (\omega_i + \omega_j) \quad (25)$$

$$M_{ij} = 2 M_i M_j / (M_i + M_j) \quad (26)$$

$$\kappa_{ij} = (\kappa_i \kappa_j)^{1/2} \quad (27)$$

where ξ_{ij} and ζ_{ij} in eq 23 and 24 are binary interaction parameters which are set equal to unity for most systems. However, for those systems which contain polar and hydrogen-bonding substances, or components with large differences in molecular structure, the binary interaction parameters are important for the viscosity and thermal conductivity predictions, and their numerical values could differ for viscosity and thermal conductivity.

The mixing rules and combining rules using values of unity for binary interaction parameters have been tested

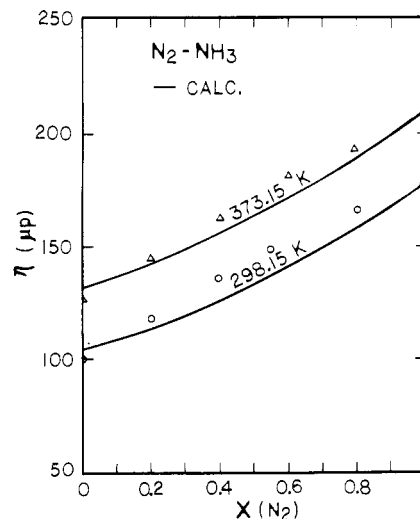


Figure 5. Comparison of calculated and experimental viscosity for N_2 - NH_3 dilute gas mixture. Data from Hongo (1977).

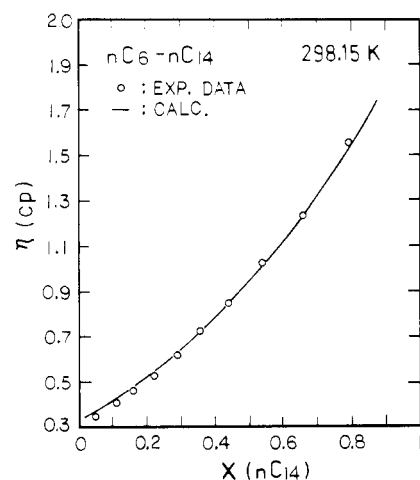


Figure 6. Comparison of calculated and experimental viscosity for n - C_6 - n - C_{14} liquid mixture. Data from Heric and Brewer (1967).

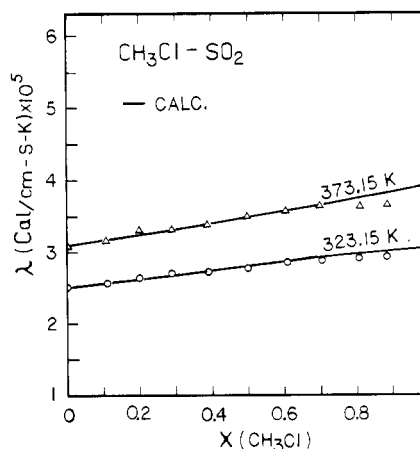


Figure 7. Comparison of calculated and experimental thermal conductivity for CH_3Cl - SO_2 dilute gas mixture. Data from Maczek and Gray (1969).

for the predictions of viscosity and thermal conductivity of over 40 binary mixtures of dilute gas systems and 80 dense gas/liquid systems including polar, nonpolar, and associated substances. Figures 5-8 compare the calculated results with the experimental values for some of these binary systems. The results in Table VI show that these mixing rules can be used with reasonable confidence for

Table V. Comparisons of Calculated and Experimental Thermal Conductivities for Pure Fluids

fluid	data no.	temp range, K	pressure range, bar	deviation, %		ref ^a
				AAD	max	
methane	367	119-726	1-1247	2.90	24.11	1,2,3,14,19, ^b 20 ^b
ethane	196	199-800	1-1194	4.23	15.35	2,4,5,21 ^b
propane	152	112-444	1-674	4.30	-10.93	6,7,22 ^b
<i>n</i> -butane	76	277-444	1-345	4.12	-8.96	8,15, ^b 20 ^b
<i>n</i> -pentane	100	146-444	1-345	5.14	-10.93	9,10,15,16,22 ^b
<i>n</i> -hexane	171	273-633	1-500	4.92	11.59	10,16,22 ^b
<i>n</i> -heptane	175	192-633	1-500	3.85	-9.27	10,15,16,22, ^b 23 ^b
<i>n</i> -octane	171	273-633	1-500	2.41	-14.27	10,15,16,22, ^b 23 ^b
<i>n</i> -nonane	15	253-413	1	4.18	-7.20	10,16,22, ^b 23 ^b
<i>n</i> -decane	20	253-433	1	4.19	-6.51	10,16,22, ^b 23, ^b 24 ^b
<i>n</i> -dodecane	17	273-473	1	3.78	-13.64	10,16,25 ^b
<i>n</i> -tridecane	12	273-493	1	1.96	-6.16	10,26 ^b
<i>n</i> -tetradecane	12	293-513	1	3.79	-9.79	10,27, ^b 28 ^b
<i>n</i> -pentadecane	13	293-533	1	3.91	17.61	10,28 ^b
<i>n</i> -hexadecane	13	313-553	1	2.86	-8.55	10,29 ^b
<i>n</i> -heptadecane	14	313-573	1	3.16	-7.86	10,29 ^b
<i>n</i> -octadecane	14	313-573	1	3.67	6.02	10,29 ^b
<i>n</i> -eicosane	14	313-573	1	2.21	-6.10	10,30 ^b
isobutane	124	193-413	1-490	4.81	15.10	10,11 ^b
benzene	29	283-450	1-6	6.03	-13.85	10,16,23, ^b 31 ^b
toluene	13	193-373	1	8.58	-18.28	10,31 ^b
<i>o</i> -xylene	31	293-626	1-604	7.72	-13.61	10,31 ^b
<i>m</i> -xylene	64	293-615	1-600	8.06	-10.91	10,31 ^b
<i>p</i> -xylene	19	293-453	1-597	7.03	-9.52	10,16, ^b 23, ^b 31 ^b
nitrogen	60	298-348	6-1015	7.30	-16.20	3,17,18,32 ^b
oxygen	35	80-180	1-500	4.72	11.72	10,19 ^b
carbon dioxide	22	300.65	6-59	5.49	18.11	3,19 ^b
sulfur dioxide	20	200-400	sat.	3.49	10.52	12
ammonia	95	300-500	1-100	4.74	-13.85	10
ethyl ether	2	273-293	1	7.70	8.28	10
chloroform	21	200-400	1	6.74	15.81	12
hydrogen chloride	44	278-323	40-120	6.78	-12.84	13
dichlorofluorene methane	21	232-450	0.1-13	3.29	7.39	10
methanol	14	290-430	1-25	7.08	-14.06	10,16 ^b
ethanol	25	213-420	1-10	2.13	-5.90	10,16 ^b
1-propanol	16	300-470	1-20	5.86	-14.73	10,16 ^b
water	319	273-973	1-500	8.33	-21.65	10,33 ^b

^a Data references: (1) Mani (1971), (2) Le Neindre et al. (1969), (3) Clifford et al. (1979), (4) Lenoir et al. (1953), (5) Guereca et al. (1967), (6) Carmichael et al. (1968a,b), (7) Roder and Nieto de Castro (1982), (8) Carmichael and Sage (1964), (9) Carmichael et al. (1969), (10) Vargaftik (1975), (11) Kazaryan and Ryabtsev (1969), (12) Touloukian et al. (1975), (13) Ziebland and Needham (1968), (14) Carmichael et al. (1966), (15) Kandiyoti et al. (1972), (16) Mallan et al. (1972), (17) Tufeu and Le Neindre (1980), (18) Moszynski and Singh (1973), (19) Johnston and Grilly (1946), (20) Ikenberry and Rice (1963), (21) Carmichael et al. (1963), (22) Brykov et al. (1970), (23) Ogiwara et al. (1980), (24) Carmichael and Sage (1967), (25) Sakiadis and Coates (1957), (26) Mustafaev (1972a), (27) Mustafaev (1972b), (28) Bogatov et al. (1969), (29) Mustafaev (1973), (30) Rastorguev et al. (1974), (31) Rastorguev and Pugach (1970), (32) Uhlir (1952), (33) Venart (1965). ^b Data sources not included in the calculation.

Table VI. Average Absolute Deviations of Calculated Viscosities and Thermal Conductivities from Experimental Data for Dilute Gas Binary Mixtures

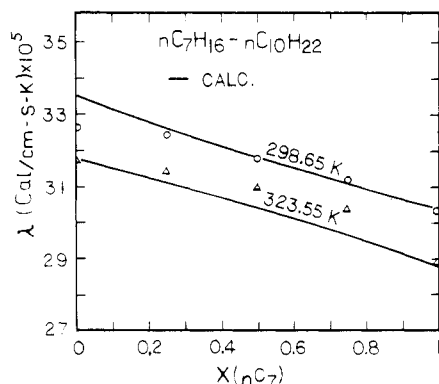
property	mixture type	<i>n</i>	AAD, %	ref
viscosity	nonpolar-nonpolar	309	1.63	Kestin and Nagashima (1964), Kestin and Yata (1968), Kestin and Wakeham (1970), Trautz and Sorg (1931), Abe et al. (1979)
	nonpolar-polar	669	4.75	Chakraborti and Gray (1966), Tanaka et al. (1977), Hongo and Iwasaki (1977), Iwasaki et al. (1964)
	polar-polar	64	3.25	Chakraborti and Gray (1965)
	associated-associated	19	3.29	Silgado and Storroy (1950)
thermal conductivity	nonpolar-nonpolar	148	2.09	Chueng et al. (1962), Smith et al. (1960), Thornton (1960), Kestin and Wakeham (1970)
	nonpolar-polar	154	4.64	Maczek and Gray (1970)
	polar-polar	66	3.10	Maczek and Gray (1969)

low-pressure gas mixtures because the deviations generally do not exceed 4% AAD. Table VII summarizes the predicted results for dense gas and liquid binary mixtures. These mixing rules when applied to nonpolar mixtures predict to within 9% AAD for 1585 viscosity data and 5% AAD for 234 thermal conductivity data. This range of accuracy is generally acceptable for most engineering design. Higher deviations appear for those systems such as C₁-*n*-C₁₀ benzene-*n*-C₁₆, which contain components of significantly different molecular volumes and shapes. However, when the binary interaction parameters are determined from data instead of being unity, the devia-

tions for the viscosity and thermal conductivity calculations are reduced significantly. For polar and associating systems, the number of data points considered is not enough to draw definitive conclusions. The effects of polar and hydrogen-bonding forces on the transport properties of mixtures are complicated and most theoretical treatments are still intractable. The mixing rules proposed for the dipole moment (μ) and the associating parameter (κ) are quite arbitrary in that the induced dipolar effect is ignored, leading to a gross oversimplification of these complicated phenomena, and thus, few encouraging results could be expected. Some other models, however, such as

Table VII. Average Absolute Deviations of Calculated Viscosities and Thermal Conductivities from Experimental Data for Dense Gas and Liquid Mixtures

property	mixture type	n	AAD, %	ref
viscosity	nonpolar-nonpolar	1585	9.19	Lee (1965), Huang et al. (1967), Cambell (1941), Lee et al. (1966), Bagziz (1971), Dewitt and Thodos (1966a,b), Bennett (1969), Chuang et al. (1976), Heric and Brewer (1967), Dixon (1959), Trevoy and Drickamer (1949), Ling and Van Winkle (1958)
	polar-associated	62	8.14	Hafez and Hartland (1976), Vitagliano et al. (1973)
thermal conductivity	nonpolar-nonpolar	234	4.73	Carmichael et al. (1968a,b), Ogiwara et al. (1980), Christensen and Fredenslund (1979), Fleeter et al. (1980), Parkinson (1974), Jamieson et al. (1975)
	nonpolar-polar	14	8.11	Jamieson et al. (1975), Jamieson and Hasting (1968)
	polar-polar	27	8.38	Jamieson and Irving (1974)
	polar-associated	35	6.79	Jamieson et al. (1975), Jamieson and Irving (1974)

**Figure 8.** Comparison of calculated and experimental thermal conductivity for n -C₇- n -C₁₀ liquid mixture. Data from Ogiwara et al. (1980).

the local-composition model, which were derived for the thermodynamic properties of polar fluid mixtures, have been shown to be applicable also for the transport properties of polar systems (Rowley, 1982).

Calculation Procedure. In order to cover all fluid states, the viscosity and thermal conductivity are correlated as functions of temperature and density in eq 10 and 12. For most engineering design, only temperature and pressure are known. Therefore, eq 10 and 12 have to be integrated with equations of state (EOS) to obtain the fluid density at a given temperature and pressure. In this work, the BWR-S-EOS (Starling, 1973) and a new generalized equation of state for nonpolar and polar fluids developed by Chung et al. (1984a, 1985) were employed to calculate fluid densities when only temperature and pressure were reported in published data. Other generalized equations of state such as the Lee-Kesler correlation (1975) and Twu correlation (1983) could have been used as well, since these EOS have also been found to be accurate for density predictions of most petroleum fluids.

When the density is known, the viscosity and thermal conductivity calculations are straightforward. Input parameters consist of the critical temperature, volume, acentric factor, and molecular weight for nonpolar substances; and dipole moment for polar substances. In addition to these parameters, an empirically determined parameter, κ , is also needed for associating substances. For pure fluids, the potential constants, σ and ϵ , are calculated from eq 4 and 5 using the critical temperature and volume, respectively. For mixtures, the mixing rules associated with the combining rules are applied to obtain the mixture's critical temperature (T_{cm}), volume (V_{cm}), acentric factor (ω_m), dipole moment (μ_m), and associating constant (κ_m) from the corresponding values of pure components. Having known all these parameters, the reduced temperature (T^*) and density (Y) are calculated and directly put in eq 10 for viscosity and in eq 12 for thermal conductivity calculations. For thermal conductivity calculations, ideal

gas heat capacity (C_v) is calculated from available correlations.

Conclusions

This work presents a predictive method to estimate the viscosity and thermal conductivity of polar, nonpolar, and associating pure fluids and mixtures over wide ranges of fluid states—from dilute gas to dense liquid. The calculation procedure involved is simple and straightforward. It requires only the critical temperature, volume, and acentric factor for pure fluids as input for the property predictions of nonpolar pure fluids and their mixtures. For polar fluids, the dipole moment is required as well. To extend the correlations to associating fluids, an association parameter determined from transport property data has been introduced to account for the effects of association.

Extensive testing with experimental data has shown the superiority of this method for the viscosity and thermal conductivity predictions for low-pressure gases; besides, the predicted results for dense gases and liquids are also in good agreement with experimental data. On average, the deviations of predicted values of pure fluids from the experimental results are about 4% for viscosity and 6% for thermal conductivity. For mixtures, the proposed method has been shown to be satisfactory for most industrial calculations. It is believed that the present work provides viscosity and thermal conductivity correlations for the broadest range of fluids within a single correlation framework.

Acknowledgment

We acknowledge the support by the National Science Foundation for this research (Grant ENG77-21551). We also thank Professor Robert C. Reid for his valuable comments.

Nomenclature

C_v = ideal gas heat capacity at constant volume, cal/(mol·K)
 D = internal self-diffusion coefficient, cm²/s
 k = Boltzmann constant
 M = molecular weight
 R = universal gas constant
 T = absolute temperature, K
 T_c = critical temperature, K
 V_c = critical volume, cm³/mol
 Z = collision number

Greek Symbols

$\beta = \eta/\rho D$ = diffusion term
 ϵ = energy potential parameter
 η = shear viscosity, g/(cm·s)
 η_0 = dilute gas shear viscosity, g/(cm·s)
 κ = association parameter
 λ = thermal conductivity, cal/(s·cm·K)
 λ_0 = dilute gas thermal conductivity
 μ = dipole moment

ρ = density
 σ = distance potential parameter
 ω = Pitzer's acentric factor
 Ω^* = reduced collision integral
 ξ, ζ = binary interaction parameters

Literature Cited

- Abe, J.; Kestin, J.; Khalifa, H. E.; Wakeham, W. A. *Physica* **1979**, *97A*, 296.
- Agae, N. A.; Yusibova, A. D. *Gazov. Prom.* **1969**, *14*(3), 41.
- Aly, F. A.; Lee, L. L. *Fluid Phase Equilib.* **1981**, *6*, 169.
- Bagziz, L. D. Master Thesis, Oklahoma State University at Stillwater, 1971.
- Barua, A. K.; Afzal, M.; Flynn, G. P.; Ross, J. J. *J. Chem. Phys.* **1964**, *41*, 374.
- Bennett, S. E. Master Thesis, Oklahoma State University at Stillwater, 1969.
- Bleakney, W. B. *J. Appl. Phys.* **1932**, *3*(3), 123.
- Bogatov, G. F.; Rastorguev, Yu. L.; Grigor'ev, B. A. *Khim. Tekhnol. Topl. Masel.* **1969**, *14*, 31.
- Boon, J. P.; Legros, J. C.; Thomas, G. *Physica* **1967**, *33*, 547.
- Brykov, V. P.; Mukhamedzyanov, G. Kh.; Usmanov, A. G. *J. Eng. Phys. (Belgrade)* **1970**, *18*, 62.
- Cambell, A. W. *Can. J. Res.* **1941**, *19B*, 143.
- Carmichael, L. T.; Sage, B. H. *J. Chem. Eng. Data* **1964**, *9*, 511.
- Carmichael, L. T.; Sage, B. H. *J. Chem. Eng. Data* **1967**, *12*, 210.
- Carmichael, L. T.; Berry, V.; Sage, B. H. *J. Chem. Eng. Data* **1963**, *8*, 281.
- Carmichael, L. T.; Jacobs, J.; Sage, B. H. *J. Chem. Eng. Data* **1968a**, *13*, 489.
- Carmichael, L. T.; Jacobs, J.; Sage, B. H. *J. Chem. Eng. Data* **1968b**, *13*, 40.
- Carmichael, L. T.; Jacobs, J.; Sage, B. H. *J. Chem. Eng. Data* **1969**, *14*, 31.
- Carmichael, L. T.; Reamer, H. H.; Sage, B. H. *J. Chem. Eng. Data* **1966**, *11*, 52.
- Chakraborti, P. K.; Gray, P. *Trans. Faraday Soc.* **1965**, *61*(11), 2422.
- Chakraborti, P. K.; Gray, P. *Trans. Faraday Soc.* **1966**, *62*(7), 1769.
- Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non-uniform Gases*; Cambridge University Press: Cambridge, London, 1952.
- Christensen, P. L.; Fredenslund, A. *J. Chem. Eng. Data* **1979**, *24*, 281.
- Chuang, S.; Chapple, P. S.; Kobayashi, R. *J. Chem. Eng. Data* **1976**, *21*, 403.
- Chueng, H.; Bromley, L. A.; Wilke, C. R. *AIChE J.* **1962**, *8*, 221.
- Chung, T. H.; Khan, M. M.; Lee, L. L.; Starling, K. E. *Fluid Phase Equilib.* **1984a**, *17*, 351.
- Chung, T. H.; Lee, L. L.; Starling, K. E. *Ind. Eng. Chem. Fundam.* **1984b**, *23*, 8.
- Chung, T. H.; Li, M. H.; Lee, L. L.; Starling, K. E. *Fluid Phase Equilib.* **1985**, *24*, 221.
- Clifford, A. A.; Kestin, J.; Wakeham, W. A. *Physica* **1979**, *97A*, 287.
- Day, R. K. *Phys. Rev.* **1932**, *40*, 281.
- DeWitt, K. J.; Thodos, G. *Physica* **1966a**, *32*, 1459.
- DeWitt, K. J.; Thodos, G. *Can. J. Chem. Eng.* **1966b**, *44*, 148.
- Diller, D. E. *Physica* **1980**, *104A*, 417.
- Diller, D. E. Proc. 8th ASME Symp. on Thermophys. Property, ASME, New York, 1981.
- Dixon, J. A. *J. Chem. Eng. Data* **1959**, *4*, 289.
- Doolittle, A. K.; Peterson, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2145.
- Dymond, J. H.; Young, K. J. *Int. J. Thermophys.* **1980**, *1*, 331.
- Dymond, J. H.; Young, K. J.; Isdale, J. D. *Int. J. Thermophys.* **1980**, *1*, 345.
- Ely, J. F.; Hanley, H. J. M. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 323.
- Ely, J. F.; Hanley, H. J. M. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 90.
- Fakeeha, A.; Kache, A.; Rehman, Z. U.; Shoup, Y.; Lee, L. L. *Fluid Phase Equilib.* **1983**, *11*, 225.
- Fleeter, R.; Kestin, J.; Wakeham, W. A. *Physica* **1980**, *103A*, 521.
- Flynn, G. P.; Hanks, R. V.; Lemaire, N. A.; Ross, J. J. *J. Chem. Phys.* **1963**, *38*, 154.
- Giddings, J. G.; Kao, J. T. F.; Kobayashi, R. *J. Chem. Phys.* **1966**, *45*, 578.
- Goldman, K. *Physica* **1963**, *29*, 499.
- Golubev, I. F. *Viscosity of Gases and Gas Mixtures*; Fizmatgiz: Moscow, 1959. (Israel program for scientific Translation (1970)).
- Gonzalez, M. H.; Bukacek, R. F.; Lee, A. L. AIME, 1966; Paper SPE-1483.
- Gonzalez, M. H.; Lee, A. L. *J. Chem. Eng. Data* **1966**, *11*, 357.
- Gracki, J. A.; Flynn, G. P.; Ross, J. J. *J. Chem. Phys.* **1969**, *51*, 3856.
- Gubbins, K. E. In *Specialist Periodical Reports in Statistical Mechanics*; Singer, K., Ed.; The Chemical Society: London, 1973; Vol. 1, p 194.
- Guereca, R. A.; Richardson, H. P.; Gordon, J. L. Report 8317, 1967; Bureau of Mines, Amarillo, TX.
- Hafex, M.; Hartland, S. *J. Chem. Eng. Data* **1976**, *21*, 179.
- Haile, J. M.; Mo, K. C.; Gubbins, K. E. *Adv. Cryog. Eng.* **1976**, *21*, 501.
- Hanley, H. J. M. "Prediction of the Thermal Conductivity of Fluids Mixtures". In *Proceedings of the 7th Symposium on Thermophysical Properties*; ASME: New York, 1977; p 668.
- Haynes, W. M. *Physica* **1973**, *70*, 410.
- Haynes, W. M. *Physica* **1974**, *76*, 1.
- Haynes, W. M. *Physica* **1977**, *89A*, 569.
- Helfand, E.; Rice, S. A. *J. Chem. Phys.* **1960**, *32*, 1642.
- Heric, E. L.; Brewer, J. G. *J. Chem. Eng. Data* **1967**, *12*, 574.
- Hongo, M. *Rev. Phys. Chem. Jpn.* **1979**, *49*(1), 11.
- Hongo, M.; Iwasaki, H. *Rev. Phys. Chem. Jpn.* **1977**, *47*(2), 90.
- Huang, E. T. S.; Swift, G. W.; Kurata, F. *AIChE J.* **1966**, *12*, 932.
- Huang, E. T. S.; Swift, G. W.; Kurata, F. *AIChE J.* **1967**, *13*, 846.
- Ikenberry, L. D.; Rice, S. A. *J. Chem. Phys.* **1963**, *39*, 1561.
- Iwasaki, H.; Kestin, J.; Nagashima, A. *J. Chem. Phys.* **1964**, *40*, 2988.
- Iwasaki, H.; Takahashi, M. *Rev. Phys. Chem. Jpn.* **1968**, *38*(1), 18.
- Jamieson, D. T.; Hasting, E. H. Proc. 8th Conf. on Therm. Cond., Purdue University, West Lafayette, IN, 1968; p 631.
- Jamieson, D. T.; Irving, J. B. Adv. in Therm. Cond. XII. International Conference on Thermal Conductivity, University of Missouri, Rolla, 1974; p 185.7.
- Jamieson, D. T.; Irving, J. B.; Tudhope, J. S. "Liquid Thermal Conductivity—A Data Survey to 1973". National Engineering Laboratory Report 601, 1975; Her Majesty Stationary Office, Edinburgh, England.
- Johnston, H. L.; Grilly, E. R. *J. Chem. Phys.* **1946**, *14*, 233.
- Kandiyoti, R.; McLaughlin, E.; Pittman, J. F. T. *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 860.
- Kazaryan, V. A.; Ryabtsev, N. I. *Gazov. Delo* **1969**, *10*, 27.
- Kestin, J.; Leidenfrost, W. *Thermodynamic and Transport Properties of Gases, Liquids, and Solids*; McGraw-Hill: New York, 1959; p 321.
- Kestin, J.; Leidenfrost, W. *Physica* **1969**, *25*, 1033.
- Kestin, J.; Nagashima, A. *J. Chem. Phys.* **1964**, *40*, 3648.
- Kestin, J.; Wakeham, W. A. Proc. 5th ASME Symp. on Thermophys. Property, ASME, New York, 1970; p 56.
- Kestin, J.; Whitelaw, J. H. *Physica* **1963**, *29*, 335.
- Kestin, J.; Yata, J. *J. Chem. Phys.* **1968**, *49*, 4780.
- Kestin, J.; Paykog, E.; Sengers, J. V. *Physica* **1971**, *54*, 1.
- Lee, A. L. "Viscosity of Light Hydrocarbons". Monography on API Research Project 65, 1965; American Petroleum Institute, New York.
- Lee, A. L.; Ellington, R. T. *J. Chem. Eng. Data* **1965a**, *10*, 101.
- Lee, A. L.; Ellington, R. T. *J. Chem. Eng. Data* **1965b**, *10*, 346.
- Lee, B. I.; Kesler, M. G. *AIChE J.* **1975**, *21*, 510.
- Lee, A. L.; Gonzalez, M. H.; Eakin, B. E. *J. Chem. Eng. Data* **1966**, *11*, 281.
- Lee, L. L.; Mo, K. C.; Starling, K. E. *Bunsen-Ges. Phys. Chem.* **1977**, *81*, 1044.
- Leland, T. W.; Rowlinson, J. S.; Sather, G. A. *Trans. Faraday Soc.* **1968**, *64*, 1447.
- Le Neindre, B.; Tufeu, R.; Bury, P.; Johannin, P.; Vodar, B. In *Proceeding of the 8th Conference on Thermal Conductivity*; Plenum: New York, 1969; p 229.
- Lenoir, J. M.; Junk, W. A.; Comings, E. W. *Chem. Eng. Prog.* **1953**, *49*, 539.
- Ling, T. D.; Van Winkle, M. *Ind. Eng. Chem. Fundam.* **1958**, *3*, 88.
- Lipkin, M. R.; Davison, J. A.; Kurtz, S. S.; Jr. *Ind. Eng. Chem.* **1942**, *34*(8), 976.
- Maczek, A. O. S.; Gray, P. *Trans. Faraday Soc.* **1969**, *65*(6), 2473.
- Maczek, A. O. S.; Gray, P. *Trans. Faraday Soc.* **1970**, *66*(1), 127.
- Mallan, G. M.; Michaelian, M. S.; Lockhart, F. J. *J. Chem. Eng. Data* **1972**, *17*, 412.
- Mani, N. Ph.D. Dissertation, University of Calgary, Calgary, Alberta, Canada, 1971.
- McCoubrey, J. C.; Singh, N. M. *J. Phys. Chem.* **1963**, *67*, 517.
- Medani, M. S.; Hasan, M. A. *Can. J. Chem. Eng.* **1977**, *55*, 203.
- Mo, K. C.; Gubbins, K. E. *Molec. Phys.* **1976**, *31*, 825.
- Moszynski, J. R.; Singh, B. P. Proc. 6th ASME Symp. on Thermophys. Property, ASME, New York, 1973; p 22.
- Mustafaev, R. A. *Teplofiz. Vys. Temp.* **1972a**, *10*, 906.
- Mustafaev, R. A. *Izv. Vyssh. Ucheb. Zaved., Neft Gaz* **1972b**, *15*, 20.

- Mustafaev, R. A. *Inzh. Fiz. Zh.* **1973**, *24*, 663.
- Nederbragt, G. W.; Boelhouwer, J. W. M. *Physica* **1947**, *13*, 305.
- Neufeld, P. D.; Janzen, A. R.; Aziz, R. A. *J. Chem. Phys.* **1972**, *57*, 1100.
- Ogiwara, K.; Aral, Y.; Saito, S. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 295.
- Parckinson, W. J. Ph.D. Dissertation, University of Southern California, Los Angeles, 1974.
- Passut, C. A.; Danner, R. P. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 543.
- Rappenecher, K. Z. *Phys. Chem.* **1910**, *72*, 695.
- Rastorguev, Yu. L.; Keramidi, A. S. *Fluid Mech.-Sov. Res.* **1974**, *3*, 156.
- Rastorguev, Yu. L.; Pugach, V. V. *Izv. Vyssh. Ucheb. Zaved., Neft Gaz.* **1970**, *13*, 69.
- Rastorguev, Yu. L.; Bogatov, G. F.; Grigor'ev, B. A. *Khim. Tekhnol. Topl. Masel* **1974**, *9*, 54.
- Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
- Roder, H. M.; Nieto de Castro, C. A. *J. Chem. Eng. Data* **1982**, *27*, 12.
- Rowley, R. L. *Chem. Eng. Sci.* **1982**, *37*, 897.
- Rowlinson, J. S.; Watson, I. D. *Chem. Eng. Sci.* **1969**, *24*, 1565.
- Saji, Y.; Kobayashi, R. *Cryogenics* **1964**, *4*, 139.
- Sakiadis, B. C.; Coates, J. *AIChE J.* **1957**, *3*, 121.
- Silgado, R. B.; Storroy, J. A. *J. Soc. Chem. India* **1950**, *69*(8), 261.
- Smith, W. J. S.; Durbin, L. O.; Kobayashi, R. *J. Chem. Eng. Data* **1960**, *5*, 316.
- Starling, K. E. Ph.D. Dissertation, Illinois Institute of Technology, Chicago, 1962.
- Starling, K. E. *Fluid Thermodynamic Properties for Light Petroleum Systems*; Gulf: Houston, TX, 1973.
- Steele, W. A.; Hanley, H. J. M., Eds. *Transport Phenomena in Fluids*; Marcel Dekker: New York, 1969; p 209.
- Stephan, K.; Lucas, K. *Viscosity of Dense Fluids*; Plenum: New York and London, 1979.
- Tanaka, Y.; Kubota, H.; Makita, T.; Okazaki, H. *J. Chem. Eng. Jpn.* **1977**, *10*(2), 83.
- Tham, M. J.; Gubbins, K. E. *Ind. Eng. Chem. Fundam.* **1969**, *8*, 791.
- Tham, M. J.; Gubbins, K. E. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 63.
- Thornton, E. *Proc. R. Phys. Soc. (London)* **1960**, *76*, 104.
- Touloukian, Y. S.; Liley, P. E.; Saxena, S. C. *Thermophysical Properties of Matter*; IFI/Plenum: New York-Washington, 1975; Vol. 3.
- Trautz, M.; Sorg, K. G. *Ann. Phys.* **1931**, *10*, 8190.
- Trevo, D. J.; Drickamer, H. G. *J. Chem. Phys.* **1949**, *17*, 582.
- Tufeu, R.; Le Neindre, B. *Int. J. Thermophys.* **1980**, *1*, 375.
- Twu, C. H. *Fluid Phase Equilib.* **1983**, *11*, 65.
- Uhlir, A., Jr. *J. Chem. Phys.* **1952**, *20*, 463.
- Van Itterbeek, V. A.; Van Paemel, O. *Physica* **1941**, *8*(1), 133.
- Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*; Wiley: New York, 1975.
- Venart, J. E. S. "Advances in Thermophysical Properties at Extreme Temperature and Pressures". 3rd ASME Symp. on Thermophys. Properties, ASME, New York, 1965; p 237.
- Vitagliano, V.; Zagari, A.; Sartorio, R. *J. Chem. Eng. Data* **1973**, *18*, 370.
- Yusibova, A. D.; Agaev, N. A. *Gazov. Prom.* **1969**, *14*(6), 46.
- Ziebland, H.; Needham, D. P. Proceedings of the 4th Symposium on Thermophysical Properties, ASME, New York, 1968; p 296.
- Zwanzig, R. *Ann. Rev. Phys. Chem.* **1965**, *16*, 67.

Received for review May 18, 1987

Accepted October 2, 1987

Thermal Energy Storage by Agitated Capsules of Phase Change Material. 1. Pilot Scale Experiments

Zeki Z. Sozen,[†] John R. Grace,* and Kenneth L. Pinder

Department of Chemical Engineering, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

Segregation due to incongruent melting has severely limited application of Glauber's salt as a phase change energy storage material. A 96% Glauber's salt/4% borax mixture was encapsulated in 25-mm-diameter hollow spheres and agitated in a liquid fluidized bed of diameter 0.34 m. The heat storage efficiency was improved by increasing the superficial water velocity and by decreasing the cooling rate. Heating rate had little effect. Fluidization provided enhanced heat transfer to or from the storage medium and resulted in a steady-state heat storage efficiency of about 60% after repeated heating and cooling cycles. The heat storage efficiency decreased to 38% of the theoretical capacity in only seven cycles under fixed bed conditions, but most of the original capacity was recovered within three cycles when these capsules were refluidized.

In space heating and domestic hot water systems, it is desirable to store energy as heat (thermal energy) since transformation of energy from one form to another results in a loss of available energy. The simplest way of storing thermal energy is as sensible heat where a material absorbs energy by increasing its temperature without undergoing any change of phase. However, thermal energy storage by phase change energy (latent heat) of a suitable material has the advantage of higher energy density (giving considerably smaller volumes) and relatively isothermal behavior (Telkes, 1975). It is possible in principle to use any reversible change with high heat of absorption or release, but solid-liquid phase changes are generally preferred for space heating and domestic hot water needs.

A number of studies (Lane et al., 1975, 1976; Heine and Abhat, 1978; Telkes, 1980; Fellchenfeld and Sarig, 1985)

have been performed to find the most promising phase change materials (PCM) for thermal energy storage (TES). Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is one of the most extensively studied phase change materials for solar energy storage because of its low price, suitable phase change temperature, high latent heat, and availability as a suitable nucleating agent (borax) (Telkes, 1952). The major problem associated with Glauber's salt is segregation due to incongruent melting (Hodgins and Hoffman, 1955). About 15 wt % of the mass of Glauber's salt forms insoluble anhydrous Na_2SO_4 crystals in a saturated Na_2SO_4 solution upon melting. The anhydrous Na_2SO_4 crystals precipitate to the bottom because their density of 2680 kg/m^3 is considerably larger than that of the saturated solution (Telkes, 1980). During cooling, anhydrous Na_2SO_4 crystals at the top of the precipitate re-form Glauber's salt crystals, blocking diffusion of water to the inner part of the precipitate and preventing the remaining anhydrous Na_2SO_4 crystals from rehydrating. The result is a loss in

[†] Present address: Yasar Holding Company, Sehiti Fethi Bey Caddesi No. 120, Alsancak 35210, Izmir, Turkey.