

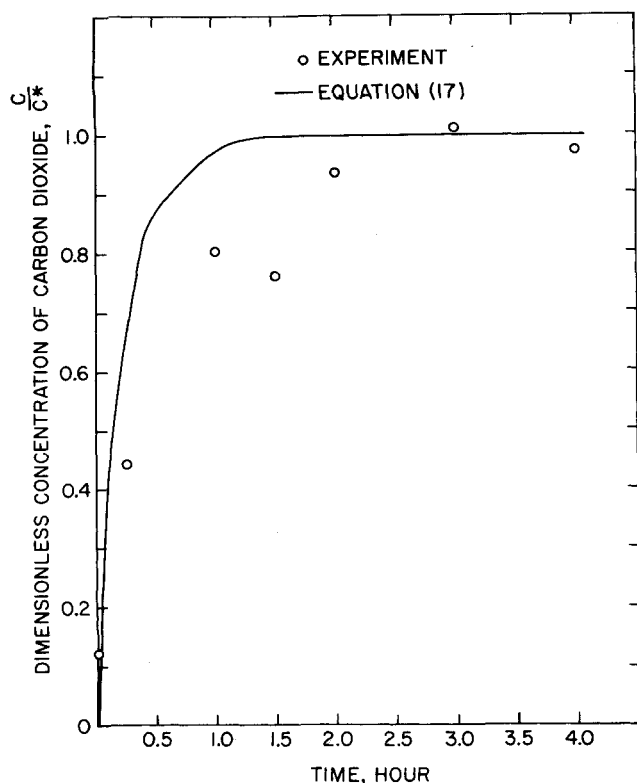


Fig. 1. Mass transfer from swarms of bubbles or drops with chemical reactions in continuous phase.

The macroscopic absorption process can be analyzed by means of a quasi steady state approximation. Since the residence time of the bubbles is much smaller than the time scale of bulk absorption, one can use steady state mass transfer for the swarm of bubbles and unsteady state absorption for the bulk liquid phase. With this assumption, one can obtain the mass balance for the continuous phase as

$$V \frac{dc}{dt} = 4\pi a^2 N_p k_L (c^* - c) \quad (11)$$

which then gives the bulk concentration of carbon dioxide as

$$\frac{c}{c^*} = 1 - \exp\left(-\frac{3V_b}{aV} k_L t\right) \quad (12)$$

It is necessary to note here that the time scale in Equation (12) is the time of absorption in the continuous phase, while the time scale in Equation (1) is the residence time of absorption from the bubble. Equation (12) is also shown in Figure 1. In application of Equation (12), the mass transfer coefficient k_L is obtained from Equation

(9) or (10) by taking $\tau \rightarrow \infty$. Although Equation (12), which is based on the quasi steady state approximation, is a simple one, it can be used to describe a system well, as can be seen in Figure 1. The present analysis can be applied to other systems such as oxidation by oxygen or ozone and hydrogenation of hydrocarbons.

ACKNOWLEDGMENT

The authors wish to thank Jacob Pruzansky for carrying out the experiment.

NOTATION

- a = radius of bubble
- c = concentration of the continuous phase
- c^* = equilibrium concentration of the continuous phase
- c_o = initial concentration of the continuous phase
- D = molecular diffusivity in the continuous phase
- k = reaction rate constant in the continuous phase
- k_L = average mass transfer coefficient
- N_p = total number of bubbles in the absorption column
- U = translational velocity of bubble
- V = volume of continuous phase
- V_b = volume of bubbles

Greek Letters

- β = viscosity ratio defined by Equation (7)
- γ = interfacial retardation viscosity
- μ_c = viscosity of continuous phase
- μ_d = viscosity of dispersed phase
- ω = c/c^*
- Φ = volume fraction of dispersed phase

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Thermal Conductivity of Liquid Mixtures

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Several methods have been proposed to estimate the thermal conductivity of liquid mixtures; most require empirical parameters or some mixture data (Jamieson and

Hastings, 1969). Critical reviews of these methods are available (Reid et al., 1976; Tsederberg, 1965).

In developing the proposed method, the following as-

TABLE 1. THERMAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF NONELECTROLYTES*
Concentration of water, mole %, thermal conductivities in W/mK

Organic component	T, °C	0	20		40		60		80		100
		λ_{exp}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}
Methanol	0	0.209	0.232	0.230	0.267	0.263	0.323	0.314	0.414	0.402	0.565
	60	0.188	0.216	0.213	0.264	0.253	0.340	0.325	0.459	0.424	0.652
Ethanol	40	0.162	0.183	0.178	0.213	0.206	0.266	0.257	0.372	0.362	0.628
Propan-1-ol	40	0.155	0.166	0.166	0.136	0.186	0.232	0.223	0.335	0.313	0.628
Propan-2-ol	40	0.137	0.148	0.148	0.170	0.166	0.216	0.203	0.321	0.295	0.628
Glycerol	40	0.285	0.296	0.298	0.313	0.317	0.345	0.350	0.412	0.420	0.628
Acetone	40	0.154	0.166	0.166	0.190	0.185	0.234	0.224	0.335	0.314	0.628
Ethylene glycol	40	0.252	0.270	0.269	0.293	0.293	0.333	0.338	0.413	0.424	0.628
Propylene glycol	40	0.199	0.212	0.212	0.236	0.232	0.278	0.270	0.363	0.355	0.628
Formamide	40	0.352	0.368	0.373	0.394	0.402	0.434	0.444	0.501	0.517	0.628
Diethylene glycol	40	0.205	0.220	0.215	0.235	0.231	0.266	0.261	0.337	0.334	0.628
Triethylene glycol	40	0.194	0.201	0.201	0.212	0.212	0.235	0.234	0.293	0.292	0.628
Pyridine	40	0.163	0.170	0.173	0.184	0.192	0.221	0.227	0.312	0.313	0.628
Dimethyl formamide	40	0.181	0.191	0.193	0.206	0.212	0.240	0.249	0.324	0.334	0.628

* Experimental data from Rastorguev and Ganier (1967).

TABLE 2. THERMAL CONDUCTIVITY OF ORGANIC LIQUID MIXTURES* WITH LIQUID MOLAR VOLUME USED
Concentration of component 2, mole %, thermal conductivities in W/mK, temperature, 40 °C

Component		0	20		40		60		80		100
1	2	λ_{exp}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}
<i>n</i> -butanol	Glycerol	0.147	0.165	0.164	0.186	0.185	0.215	0.214	0.247	0.244	0.283
Triethylene glycol	Formamide	0.195	0.198	0.202	0.207	0.214	0.223	0.233	0.262	0.267	0.350
Methanol	Formamide	0.205	0.234	0.227	0.263	0.253	0.292	0.283	0.321	0.320	0.350
Propan-1-ol	Triethylene glycol	0.153	0.155	0.163	0.168	0.174	0.179	0.182	0.188	0.189	0.195
Propan-2-ol	Formamide	0.137	0.151	0.151	0.176	0.173	0.213	0.207	0.262	0.262	0.350
<i>n</i> -butanol	Triethylene glycol	0.147	0.160	0.159	0.170	0.169	0.181	0.179	0.188	0.187	0.195

* Experimental data from Rastorguev and Ganier (1967).

TABLE 3. THERMAL CONDUCTIVITY OF ORGANIC LIQUID MIXTURES* WITH CRITICAL MOLAR VOLUMES USED
Concentration of component 2, weight %, λ , thermal conductivities in W/mK, temperature = 0 °C

Component		0	25	50	75	100			
1	2	λ_{exp}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}	λ_{calc}	λ_{exp}
Diethylether	Methanol	0.1409	0.154	0.154	0.173	0.171	0.188	0.189	0.2096
Toluene	Diethylether	0.140	0.1407	0.1401	0.1413	0.1403	0.142	0.1406	0.1409
Benzene	Toluene	0.152	0.1465	0.1488	0.1441	0.1457	0.1451	0.1428	0.140
Acetone	Methanol	0.1711	0.1801	0.1800	0.1894	0.1889	0.1975	0.1991	0.2096
Methanol	Benzene	0.2096	0.1975	0.195	0.1722	0.180	0.1655	0.165	0.152
Toluene	Methanol	0.140	0.1521	0.155	0.1687	0.172	0.1865	0.190	0.2096
Aniline	Methanol	0.1725	0.1858	0.182	0.1898	0.192	0.2001	0.206	0.2096
Acetone	Aniline	0.1711	0.1734	0.1714	0.1759	0.1718	0.1703	0.1721	0.1725
Toluene	CCl ₄	0.140	0.130	0.1348	0.1201	0.1283	0.1107	0.1190	0.1082
CCl ₄	Tert-butanol	0.1082	0.1001	0.1090	0.1018	0.1119	0.1065	0.1129	0.1143
CCl ₄	Methanol	0.1082	0.1234	0.141	0.1510	0.172	0.1853	0.191	0.2096
CCl ₄	Acetone	0.1082	0.1185	0.130	0.1318	0.146	0.1544	0.160	0.1711
Tert-butanol	Acetone	0.1143	0.1259	0.124	0.1433	0.141	0.1592	0.156	0.1711
Toluene	Acetaldehyde	0.140	0.1495	0.153	0.1642	0.168	0.1720	0.184	0.2005

* Experimental data from Jamieson and Hastings (1969).

sumptions were made:

1. Energy transport in the liquid state occurs by collision among molecules. The collision process is due primarily to the oscillation of neighboring molecules in a quasi equilibrium state, and molecular diffusion has negligible effect except close to the vapor-liquid critical region. If a liquid mixture is remote from its critical state, it is reasonable to assume that the frequency of collision is approximately proportional to the number as well as the size of the neighboring molecules. This assumption implies that for this thermodynamic state, the approximate weighting parameter for such a collision process should be the volumetric fraction instead of the mole fraction.

2. The interaction thermal conductivity can be approximated by a harmonic mean of the pure component values.

Based on these assumptions, the liquid-mixture thermal conductivity is given as

$$\lambda_m = \sum_i \phi_i \lambda_i \quad (1)$$

where

$$\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \quad (2)$$

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \quad (3)$$

$$\sum_i \phi_i = 1 \quad (4)$$

The liquid molar volumes used in defining ϕ_i may be replaced by critical volumes for nonaqueous systems without affecting the results significantly.

METHANOL / WATER

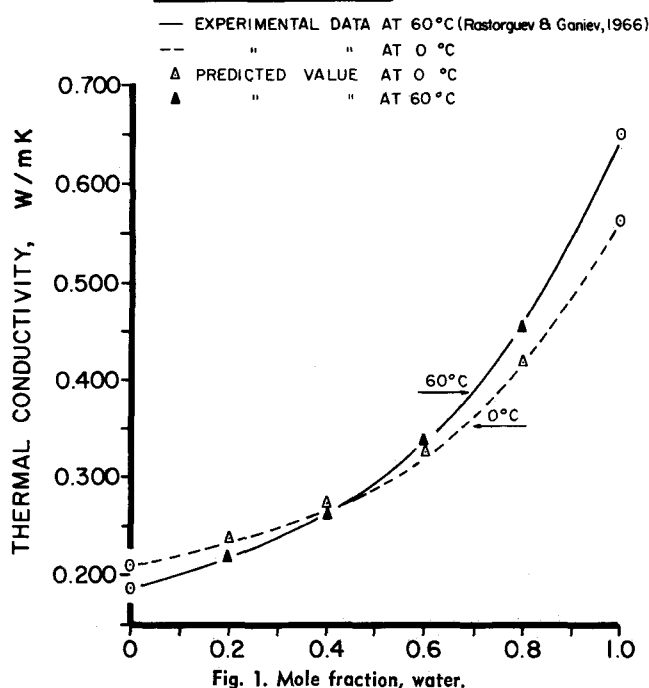


Fig. 1. Mole fraction, water.

CCl₄ / TERTBUTANOL (0°C)

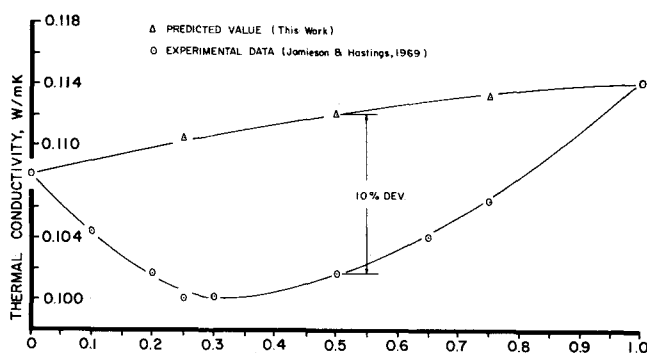


Fig. 2. Weight fraction, tertbutanol.

RESULTS

By using Equations (1) through (4), liquid thermal conductivities were calculated for a number of binary systems, and the results are shown in Tables 1 (aqueous solutions) and 2 (nonaqueous solutions). The overall deviations between calculated values of λ_m and those measured experimentally were 2.3% (Table 1) and 2.0% (Table 2). Using critical volumes in place of liquid volumes, we show deviations for organic liquid mixtures in Table 3.

TABLE 4. COMPARISON OF VARIOUS PREDICTIVE METHODS

Reference to Table 1 organic/water mixture (40°C)

	NEL	Filippov	Average absolute % deviation Arithmetic	Geometric	Harmonic
Methanol (0°C)	1.88	4.53	7.54	2.42	1.32
(60°C)	2.68	3.41	8.42	1.58	4.47
Ethanol	3.23	2.77	12.53	2.64	2.99
n-propanol	3.12	0.68	15.51	5.47	2.59
Isopropanol	2.13	0.46	17.60	5.09	4.13
Glycerol	5.12	5.43	7.53	4.44	1.71
Acetone	2.33	0.45	15.42	4.65	3.38
Ethyleneglycol	4.61	5.37	11.66	4.77	1.16
Propyleneglycol	5.70	6.35	10.34	3.86	1.68
Formamide	3.41	4.10	5.30	3.60	1.98
Diethyleneglycol	6.86	7.11	8.96	3.44	1.72
Triethyleneglycol	4.90	5.13	10.56	5.20	0.17
Pyridine	0.87	1.47	19.79	10.19	2.42
Dimethylformamide	2.07	1.44	17.64	9.53	2.78
	3.49	3.48	12.06	4.78	2.32

Reference to Table 2 organic liquid mixture (40°C)

n-butanol/glycerol	1.42	0.72	3.10	0.92	1.06
Triethyleneglycol/formamide	0.77	1.44	6.28	4.64	2.92
Methanol/formamide	2.64	4.06	0.22	1.56	2.58
n-propanol/triethylene glycol	3.02	2.46	3.77	3.58	3.18
Isopropanol/formamide	2.36	0.90	7.46	2.87	1.48
n-butanol/triethyleneglycol	2.43	3.11	0.15	0.35	0.64
	2.11	2.12	3.50	2.32	1.98

Reference to Table 3 organic liquid mixture (0°C)

Diethylene/methanol	2.82	3.66	5.01	1.11	0.79
Toluene/diethylether	0.70	0.71	0.61	0.61	0.61
Benzene/toluene	0.67	0.65	1.48	1.56	0.76
Methanol/acetone	1.84	2.27	0.78	0.51	0.37
Methanol/benzene	2.65	3.30	2.58	2.47	1.99
Methanol/toluene	1.79	2.65	3.90	3.02	1.99
Aniline/methanol	2.87	3.27	1.19	1.12	1.07
Aniline/acetone	1.57	1.56	1.53	1.52	1.57
Toluene/CCl ₄	0.87	1.35	6.92	6.58	6.02
Tert butanol/CCl ₄	7.73	7.28	9.06	9.06	8.64
CCl ₄ /methanol	4.24	5.61	14.45	13.28	9.64
Acetone/CCl ₄	2.52	3.17	15.74	9.65	8.43
Acetone/tertbutanol	3.86	4.70	1.59	1.81	2.00
Acetaldehyde/toluene	2.51	2.49	5.72	5.01	4.15
	2.62	3.05	5.04	4.09	3.43

To illustrate the proposed method, Figure 1 shows calculated and experimental liquid thermal conductivity data for the system methanol water at 0° and 60°C. Figure 2 exemplifies a limitation of Equation (1) in that it fails to predict the minimum thermal conductivities for the azeotropic liquid mixture, CCl₄/tert-butanol.

DISCUSSION

The size and the number of molecules are equally important. This can be verified by neglecting the size effect when the mole fraction is used instead of the volumetric fraction in Equation (1). If such a substitution is made, the error in the calculated values will be significantly greater than for calculations with the volumetric average used. This indicates that for energy transport in a liquid mixture, the volumetric fraction is more appropriate than the molar fraction. Equation (1), however, reduces to a molar average when the liquid molar volumes of the components are equal.

The proposed method fails to predict any minimum or maximum thermal conductivity of a mixture as a function of composition. This limitation is shown in Figure 2 for the azeotropic liquid mixture carbon tetrachloride-*t*-butanol.

To compare the accuracy of the new method with others that have been proposed, in Table 4, we show calculated absolute percent deviations from experimental data. The column marked harmonic indicates that Equations (1) through (4) of the present Note were used. Also shown are results assuming a geometric mean and an arithmetic for λ_{ij} ; that is

$$\lambda_{ij} = \sqrt{\lambda_i \lambda_j} \quad \text{geometric mean} \quad (5)$$

$$\lambda_{ij} = (\lambda_i + \lambda_j)/2 \quad \text{arithmetic mean} \quad (6)$$

Clearly, the harmonic mean choice leads to the least error.

Also shown are deviations for the NEL correlation (Jamieson and Hastings, 1969) for binary systems

$$\frac{\lambda_m - \lambda_1}{\lambda_2 - \lambda_1} = \alpha w_2^{3/2} + w_2(1 - \alpha) \quad (7)$$

where w_2 is the weight fraction of component 2 and $\lambda_2 > \lambda_1$. The adjustable parameter α was set equal to unity. In addition, the Filippov relation was tested (Filippov, 1955):

$$\frac{\lambda_m - \lambda_1}{\lambda_2 - \lambda_1} = C w_2^2 + w_2(1 - C) \quad (8)$$

w_2 was defined above, and the parameter C was chosen to equal 0.7 (Reid et al., 1976). As suggested by Reid (1976), if Equation (1) is used with the geometric mean assumption for λ_{ij} [Equation (5)] and compared to Equation (8), it can be shown that

$$C = \left| \frac{\lambda_2^{1/2} - \lambda_1^{1/2}}{\lambda_2^{1/2} + \lambda_1^{1/2}} \right| \quad (9)$$

The conclusion from the results shown in Table 4 is that the harmonic mean assumption [Equations (1) through (4)] yields estimations of λ_m which are generally more accurate than other correlations and within normal experimental error (circa $\pm 3\%$).

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NOTATION

V	= liquid molar volume
w	= weight fraction
x	= mole fraction
ϕ	= volume fraction
λ	= thermal conductivity

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The Linear Hydrodynamic Stability of Film Flow Down a Vertical Cylinder

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Film flow occurs in a variety of engineering equipment for gas-liquid contacting and in a number of industrial

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processes for coating and surface treating solid surfaces. Furthermore, wetted wall columns are widely used as laboratory absorbers and reactors for determining mass transfer coefficients and kinetic data. Engineers have been interested in the stability of this flow because of its pro-