Transport Properties of Multi-component Polar Gas Mixtures Containing Mono-, Di-, and Trimethylamines*

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The viscosity and thermal conductivity coefficients of monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA), and their binary mixtures have been measured in the temperature range 25—250 °C. In addition, determinations of thermal conductivity of ternary mixtures at 33 and 88 °C and of several quaternary mixtures (with ammonia) at 33 °C have been made. The results are discussed in the light of modern kinetic theory of gases. Finally, the coefficients of self-diffusion and mutual diffusion in binary mixtures of these gases are estimated from the experimental viscosity results.

In two previous studies[1,2] measurements of the viscosities and thermal conductivities of ammonia-monomethylamine mixtures have been reported. In the present paper, we extend these measurements to di- and trimethylamine and to binary mixtures of these gases with each other and with monomethylamine. In addition, we have made thermal conductivity measurements of some ternary mixtures of the methylamines and of some quaternary ones of these gases with ammonia. No previous studies of the transport properties of di- and trimethylamine or any of the mixtures mentioned have been reported. Furthermore, no previous work seems to have been done on the thermal conductivities of polar gas mixtures containing more than two polar gases except that of Maczek and Gray[3] on mixtures of methyl chloride, sulfur dioxide, and dimethyl ether.

Theoretical Considerations

The interaction between a pair of polar molecules may be expressed by the Stockmayer potential model: $\phi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}+\delta(\sigma/r)^{3}]$, where $\delta=(\mu^2/4\varepsilon\sigma^3)-\zeta$; μ is the dipole moment, ε and σ are the potential parameters representing the depth of the potential well and the molecular separation at zero interaction distance, respectively; and ζ is a function of the relative orientation of the colliding pair of dipoles. Monchick and Mason[4] have published the collision integrals (averaged over all relative orientations) for this potentail model and have outlined a procedure for obtaining the potential parameters (ε, σ, and $\delta_{max}=\mu^2/2\varepsilon\sigma^3$) from the experimental viscosity data. The Stockmayer model has been extended to polar gas mixtures by Mason and Monchick.[5] Simple standard combining rules, namely, $\sigma_{12}=(\sigma_1+\sigma_2)/2$, $\varepsilon_{12}=(\varepsilon_1\varepsilon_2)^{1/2}$, $\delta_{12}=(\delta_1\ \delta_2)^{1/2}$ are found to be adequate in applying this method to the gas mixtures considered here.

The viscosity of the binary gas mixtures is given by Eq. (8.2—22) of the treaties of Hirschfelder *et al.*[6] The mutual diffusion coefficients and the collision integral ratio $\langle A^*_{12}\rangle$ which appear in this equation were calculated from the tabulated collision integrals in conjunction with the above combining rules. The viscosity and the self-diffusion coefficients can be obtained from the rigorous kinetic theory expressions.[6] The self-diffusion coefficients of a pure gas can also be obtained from the relation[7,8]

$$D_{11} = (6/5)(RT/p)(\eta/M)\langle A^*_{11}\rangle, \qquad (1)$$

where R is the gas constant, T is the absolute temperature, p is the pressure, η is the viscosity coefficient, and M is the molecular weight. The values of the collision integral ratio $\langle A^*_{11}\rangle$ are very insensitive to the particular potential model chosen and to the temperature; thus Eq. (1) is essentially dependent on the gas viscosities.

Apart from the empirical or the semi-empirical methods, the mutual diffusion coefficients can be calculated from the rigorous kinetic theory expression,[6] or can be obtained from the experimental viscosities of the binary gas mixtures according to the relation due to Weissman and Mason.[7,8] This relation is analogous to Eq. (1), but involves solution of a quadratic equation in pD_{12} whose coefficients involve functions of mole fractions, molecular weights of pure gases, viscosity of the gas mixture, and collision integral ratio $\langle A^*_{12}\rangle$.

For the pure gases it is customary to express the thermal conductivity in terms of the dimensionless Eucken factor $f=\lambda M/\eta C_V$, where λ is the thermal conductivity coefficient, M is the molecular weight, η is the viscosity coefficient, and C_V is the constant volume molar heat capacity. Rigorous theory and the experiment both show that f has a value close to 2.5 for the structureless gases.[9] For polyatomic gases, however, f is less than 2.5. Eucken[10] thus proposed

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1) L. G. Burch and C. J. G. Raw, *J. Chem. Phys.*, **47**, 2798 (1967).

2) J. Gutweiler and C. J. G. *ibid.*, **48**, 2413 (1968).

3) A. O. S. Maczek and P. Gray, *Trans. Faraday Soc.*, **65**, 1473 (1969).

4) L. Monchick and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961).

5) E. A. Mason and L. Monchick, *ibid.*, **36**, 2746 (1962).

6) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., 2nd ed., New York (1964).

7) S. Weissman and E. A. Mason, *J. Chem. Phys.*, **37**, 1289 (1962).

8) E. A. Mason and T. R. Marrero, "Advances in Atomic and Molecular Physics," Ed. D. R. Bates and I. Easterman, Academic Press, New York (1970), Vol. 6, p. 155.

9) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge Press, 3rd ed., New York (1970).

10) A. Eucken, *Phys. Z.*, **14**, 324 (1913).

a simple correction: $f_E=1+(9/4)(R/C_v)$. Later, a modified Eucken formula was suggested which was based on a diffusion mechanism theory:[11] $f_{ME}=(\rho D_{11}/\eta)+(3/2)[(5/2)-(\rho D_{11}/\eta)]\ (R/C_v)$, where ρ is the density of the gas and other symbols have been previously defined. Finally, Mason and Monchick[12] have suggested a second approximation which is based on the formal kinetic theory of gases: $f_{MM}=f_{ME}-(2/\pi C_v)\text{-}[(5/2)-(\rho D_{int}/\eta)]^2\ (C_{int}/Z_{int})$, where D_{int} is the diffusion coefficient for the diffusion of the internal energy, C_{int} is the internal contribution to C_v, and Z_{int} is the collision number for relaxation of the internal modes of energy. Essentially, the only internal mode of energy for small gaseous molecules at ordinary temperatures is the rotational mode, since the vibration excitation is very small. Therefore, C_{int} may be taken as $(3/2)R$ for non-linear molecules. Z_{int}, which by the same token would be taken as Z_{rot}, can be best treated as an adjustable parameter in correlating this theory with the experimental data. D_{int}, finally, is the ordinary self-diffusion coefficient corrected for the resonant exchange of the rotational quanta of energy.

For the thermal conductivity of multi-component gas mixtures the Hirschfelder-Eucken equation may be used: $\lambda_{mix}=(\lambda_{mix})_{tr}+(\lambda_{mix})_{int}$. $(\lambda_{mix})_{tr}$ is the first approximation of the thermal conductivity of a gas mixture containing several monatomic components and is expressed by a ratio of two determinants, which is given by Eq. (8.2-43) of Ref. 6. The complication of the evaluation of this equation, however, is twofold. In fact not only must one solve a $(2n+1)\times(2n+1)$ and a $(2n)\times(2n)$ determinant for an n-component mixture, but also each of the elements of these determinants is very complicated. Mason[13] and Muckenfuss and Curtiss[14] have derived simpler formulas with the same degree of rigor as the original one. In this study we have considered Mason's, *i.e.*,

$$(\lambda_{mix})_{tr}=4\begin{bmatrix} L_{11}\cdots L_{1n} & x_1 \\ \vdots\quad\ \vdots & \vdots \\ L_{n1}\cdots L_{nn} & x_n \\ x_1\ \cdots\ x_n & 0 \end{bmatrix}\begin{bmatrix} L_{11}\cdots L_{1n} \\ \vdots\quad\ \vdots \\ L_{n1}\cdots L_{nn} \end{bmatrix}^{-1} \tag{2}$$

where,

$$L_{ii}=\frac{-4x_i^2}{[\lambda_i]_1}-\frac{16T}{25p}\times\sum_{\substack{k=1\\k\neq i}}\frac{x_ix_k[(15/2)M_i^2+(5/2)M_k^2+4M_iM_kA_{ik}^*]}{(M_i+M_k)^2[D_{ik}]_1}, \tag{3}$$

and,

$$L_{\substack{ij\\(i\neq j)}}=\left(\frac{16T}{25p}\right)\frac{x_ix_jM_iM_j(10-4A_{ij}^*)}{(M_i+M_j)^2[D_{ij}]_1}, \tag{4}$$

where $[\lambda_i]_1$ and $[D_{ij}]_1$ are the first approximations to the thermal conductivity and the mutual diffusion coefficients, respectively, and M_i and X_i are the molecular weight and the mole fraction of the component i, and other terms have their ordinary meanings. $(\lambda_{mix})_{int}$ in the Hirschfelder-Eucken expression is the contribution of the internal modes to the thermal conductivity coefficient and is given by:[15]

$$(\lambda_{mix})_{int}=\sum_i\lambda_{int\,i}\left[1+\sum_{i\neq j}\frac{D_{ii,int}x_j}{D_{ij,int}x_i}\right]^{-1}, \tag{5}$$

where $\lambda_{int,i}=\lambda_{expt,i}-[\lambda_i]_1$, and $D_{ii,int}$ is the self-diffusion coefficient of internal energy which has been equated to the ordinary diffusion coefficient by Hirschfelder.[15] $D_{ij,int}$ corresponds, accordingly, to the mutual diffusion coefficient of internal energy.

Among the several empirical formulas which have been put forward for the thermal conductivity of the mixtures, we have considered the better-know Wassiljewa equation:[16]

$$\lambda_{mix}=\sum_i\lambda_i\sum_{i\neq j}\left[1+A_{ij}\frac{x_j}{x_i}\right]^{-1}. \tag{6}$$

In the above equation λ_i is the experimental thermal conductivity coefficient of the component i. The Wassiljewa coefficients, A_{ij}'s, can be calculated from the Lindsay-Bromley approximation:[17]

$$A_{ij}=\frac{1}{4}\left[1+\left\{\frac{\eta_i}{\eta_j}\left(\frac{M_i}{M_j}\right)^{3/4}\frac{T+S_i}{T+S_j}\right\}^{1/2}\right]^2\left(\frac{T+S_{ij}}{T+S_j}\right), \tag{7}$$

where S_i is the Sutherland's coefficient (Ref. 6, p. 550) and $S_{ij}=(S_iS_j)^{1/2}$, and other symbols have their usual meanings. It will be discussed later that the use of Eqs. (2) and (5) is justified by the theoretical studies of Monchick *et al.*,[18] and by the previous experimental studies.[2,19]

Experimental

The apparatus used in the viscosity and in the thermal conductivity measurements have been described previously by Chang *et al.*[19] The viscometer was a constant volume type employing the capillary transpiration method. The thermal conductivities were measured with a "potential leads" hot wire type cell. In both cases the apparatus were placed in an oil bath and in a furnace for the measurements below and above 150 °C, respectively. The temperature could be controlled to within 0.2 °C in the lower temperature ranges and to within 0.5 °C in the higher ones. The gases were supplied by the Matheson Company (minimum purities: NH_3, 99.9%; CH_3NH_2, 98.0%; $(CH_3)_2NH$, 99.0%; $(CH_3)_3N$, 99.0%). The gas mixtures were prepared in the usual way.[1,2,19] Heat capacity data were obtained from Kobe and Harrison.[20] The computations were carried out at the Yalem Computer Center of St. Louis University using a CDC 3300 computer.

Results and Discussion

Pure Gases. In Table 1 the experimental and the theoretical viscosities of di- and trimethylamines

11) J. O. Hirschfelder, *J. Chem. Phys.*, **26**, 282 (1957).
12) E. A. Mason and L. Monchick, *ibid.*, **36**, 1622 (1962).
13) E. A. Mason, *ibid.*, **28**, 1000 (1958).
14) C. Muckenfuss and C. F. Curtiss, *ibid.*, **29**, 1273 (1958).
15) J. O. Hirschfelder, 6th Int. Symp. on Combustion (Reinhold, New York, 1957).
16) A. Wassiljewa, *Phys. Z.*, **5**, 737 (1904).
17) A. L. Lindsay and L. A. Bromley, *Ind. Eng. Chem.*, **42**, 161 (1961).
18) L. Monchick, A. N. G. Pereira, and E. A. Mason, *J. Chem. Phys.*, **42**, 3241 (1965).
19) K. C. Chang, R. J. Hesse, and C. J. G. Raw, *Trans. Faraday Soc.*, **66**, 590 (1970).
20) K. A. Kobe and R. H. Harrison, *Petr. Ref.*, **33**, (No. 11), 161 (1954).

Table 1. Calculated and experimental viscosity coefficients of dimethylamine (DMA) and trimethylamine (TMA)
η in units of 10^7 g cm^{-1} s^{-1}; η (calc) is from Eq. (8.2.-18) of Ref. 6.

Temp (°C)	DMA		TMA	
	η (exptl)	η (calc)	η (exptl)	η (calc)
25.0	924	919	912	906
50.0	983	987	961	961
75.0	1043	1057	999	1013
100.0	1103	1121	1058	1063
150.0	1220	1244	1150	1164
225.0	1397	1424	1288	1301

Table 2. Calculated and experimental thermal conductivity coefficients of dimethylamine (DMA) and trimethylamine (TMA),
λ in units of cal km^{-1} s^{-1} deg (°C)$^{-1}$; λ (calc) is according to Ref. 12.

Temp (°C)	DMA		TMA	
	λ (exptl)	λ (calc)	η (exptl)	η (calc)
37.0	3.57	4.68	3.44	4.28
88.0	5.30	6.00	4.96	5.46
133.0	6.85	7.12	6.40	6.58
188.0	8.70	8.85	8.12	8.01
237.0	10.66	10.37	9.80	9.36

are presented. Table 2 contains the corresponding thermal conductivities. In both cases the experimental data have been corrected appropriately for "slip" (in the case of viscosity) and "temperature jump" (in the case of thermal conductivity).

The Stockmayer potential parameters were found to be:

(i) for $(CH_3)_2NH$: $\sigma=5.09$ Å, $\varepsilon/k=191$ K, and $\delta_{max}=0.14$

(ii) for $(CH_3)_3N$: $\sigma=6.25$ Å, $\varepsilon/k=85$ K, and $\delta_{max}=0.065$.

The quoted values of λ_{MM} were found, as mentioned before, by treating Z_{rot} as an adjustable parameter, and then using their averaged values in the expression of f_{MM}. The averaged values were found to be 1.99 and 0.67 for dimethylamine and trimethylamine, respectively. We could have arrived at better agreement between λ_{exp} and λ_{MM} if we were using different values of Z_{rot} at each temperature. However, the extreme sensitivity of Z_{rot} to f_{exp} would make such a treatment rather unreliable. To account for the resonant exchange of rotational energy, we have employed the values of the moments of inertia[21] with other necessary constants in the appropriate formulas.[12] We have treated dimethylamine as a "prolate top" and trimethylamine as an "almost spherical top". We have found that the correction is indeed negligibly small for both gases (less than 0.01 per cent).

The self-diffusion coefficients were predicted by using the kinetic theory expression and the Eq. (1), as mentioned previously. No experimental self-diffusion data are available for comparison purposes. However, these predictions are generally quite reliable.[8] In the case of gaseous ammonia, the earlier predictions of the self-diffusion coefficient by Burch and Raw[1] were found later to be in excellent agreement with the experimental results of Baker.[22] The predicted values of the self-diffusion coefficients of di- and trimethylamines are presented in Table 3.

Table 3. Self-diffusion coefficients of dimethylamine (DMA) and trmiethylamine (TMA) at 1 atm pressure in units of cm^2 s^{-1}

Temp (°C)	DMA		TMA	
	D_{11}(theory)[a]	D_{11}Eq. (1)	D_{11}(theory)[a]	D_{11} Eq. (1)
25.0	0.0655	0.0659	0.0492	0.0496
37.0	0.0712	—	0.0530	—
50.0	0.0766	0.0764	0.0569	0.0570
75.0	0.0885	0.0880	0.0645	0.0641
88.0	0.0942	—	0.0680	—
100.0	0.100	0.0985	0.0723	0.0721
133.0	0.110	—	0.0823	—
150.0	0.126	0.123	0.0902	0.0891
188.0	0.148	—	0.104	—
225.0	0.169	0.166	0.119	0.118
237.0	0.176	—	0.123	—

a) These values were calculated from the rigorous kinetic theory expression using the Stockmayer potential parameters.

Gas Mixtures. The mutual diffusion coefficients of methylamines as obtained by the rigorous kinetic theory[6] and the Mason-Weissman[7,8] expressions are presented in Table 4. The quoted values in the case of the latter, it should be noted, are the averaged values over the concentrations at each temperature. The individual values were slightly different from each

Table 4. Mutual diffusion coefficient of methylamines* at 1 atm pressure in units of cm^2 s^{-1}

Temp (°C)	D_{12}[a]	D_{12}[b]	D_{13}[a]	D_{13}[b]	D_{23}[a]	D_{23}[b]
25.0	0.0808	0.0808	0.0698	0.0669	0.0571	0.0573
37.0	0.0870	—	0.0730	—	0.0613	—
50.0	0.0943	0.0933	0.0608	0.0774	0.0656	0.0660
75.0	0.109	0.107	0.0924	0.0966	0.0746	0.0753
88.0	0.117	—	0.0987	—	0.0800	—
100.0	0.125	0.122	0.105	0.107	0.0843	0.0872
133.0	0.139	—	0.117	—	0.100	—
150.0	0.158	0.155	0.133	0.127	0.107	0.106
188.0	0.187	—	0.150	—	0.125	—
225.0	0.215	0.210	0.179	0.171	0.143	0.143
237.0	0.221	—	0.183	—	0.149	—

* 1=monomethylamine; 2=dimethylamine; 3=trimethylamine.

a) These values are calculated from the rigorous kinetic theory expression using the mixed potential parameters for the Stockmayer model predicted by the combining rules.

b) These values are calculated using the technique of Ref. 7.

21) G. Dellepiane and G. Zerbi, *J. Chem. Phys.*, **48**, 3573 (1968). (See also: J. E. Wollarb and V. W. Lourie, *ibid.*, **48**, 5058 (1968); *ibid.*, **51**, 1580 (1969)).

22) C. E. Baker, *ibid.*, **52**, 2159 (1970).

TABLE 5. VISCOSITY COEFFICIENTS OF BINARY MIXTURES OF METHYLAMINES[a] η IN UNITS OF g cm^{-1} s$^{-1}\times 10^7$. η (calc) is from Eq. (8.2-25) of Ref. 6.

Temp (°C)	Mole fraction[b]	MMA–DMA		MMA–TMA		DMA–TMA	
		η (exptl)	η (calc)	η (exptl)	η (calc)	η (exptl)	η (calc)
25.0	0.25	928	927	918	905	916	916
	0.50	932	932	923	904	917	919
	0.75	938	937	931	915	920	922
50.0	0.25	989	991	971	959	967	969
	0.50	996	998	983	963	972	975
	0.75	1004	1006	998	979	977	980
75.0	0.25	1051	1055	1024	1040	1017	1021
	0.50	1061	1066	1043	1065	1026	1030
	0.75	1073	1077	1064	1083	1035	1039
100.0	0.25	1113	1118	1078	1085	1067	1082
	0.50	1126	1133	1103	1112	1080	1095
	0.75	1142	1147	1130	1138	1092	1105
150.0	0.25	1232	1243	1185	1167	1168	1170
	0.50	1265	1266	1221	1192	1199	1189
	0.75	1290	1283	1262	1238	1207	1206
225.0	0.25	1428	1433	1345	1318	1313	1322
	0.50	1458	1470	1393	1365	1365	1353
	0.75	1498	1507	1460	1436	1397	1379

a) MMA=monomethylamine, DMA=dimethylamine, TMA=trimethylamine.
b) Mole fraction of the lighter component.

other, and this difference was in order of the experimental uncertainties of the viscosity measurements (1%). The mutual diffusion coefficients of ammonia–dimethylamine and ammonia–trimethylamine mixtures, at 33 °C, were found to be 0.129 cm^2 s^{-1} and 0.111 cm^2 s^{-1}, respectively, according to the kinetic theory. The corresponding value for ammonia–monomethylamine mixture was extrapolated from the results of Burch and Raw.[1] These values were used in the Hirschfelder-Eucken formula for the theoretical calculations of the thermal conductivities of the quaternary mixtures. The agreement between the experimental and the predicted values of viscosities, as well as the predicted values of diffusion coefficients by the kinetic theory and the Mason-Weissman expressions, confirms the adequacy of the Stockmayer potential parameters and the simple combining rules. The thermal conductivities of the multi-component mixtures were estimated by the Hirschfelder-Eucken expression. As indicated before, $[\lambda_{tr}]_{mix}$'s were found according to the expression suggested by Mason. In all cases the self diffusion coefficients, D_{ii}, and the mutual diffusion coefficients, D_{ij}, were taken as the internal diffusion coefficients. $D_{ii,int}$ and $D_{ij,int}$, respectively. Although well-established corrections are available for the self-diffusion coefficients, no such corrections has been suggested for $D_{ij,int}$. Writing this correction as δ_{ii}, according to the notation used by Mason and Monchick,[12] then the assignment of $\delta_{ij}=(\delta_{ii}+\delta_{jj})/2$ is as good an empirical guess as any. Nevertheless, these corrections would be negligibly small for the present investigation. The corrections for inelastic collisions applied to the Hirschfelder-Eucken formula come with the use of the experimental thermal conductivities of the pure gases. By using such values, account would be taken of the inelastic as well as the resonant collisions. These considerations are justified by the theoretical studies of Monchick *et al.*,[18] and by the previous experimental measurements.[2,19]

The thermal conductivity coefficients of the binary and the ternary mixtures are also estimated by the Wassiljewa equation. The Wassiljewa coefficients, as obtained from the Lindsay-Bromely relation, are presented in Table 6. As may be seen from this table,

TABLE 6. WASSILJEWA COEFFICIENTS OF METHYLAMINES[a] AS CALCULATED FROM THE LINDSAY-BROMLEY EXPRESSION

Temp (°C)	MMA–DMA		MMA–TMA		DMA–TMA	
	A_{ij}	A_{ji}	A_{ij}	A_{ji}	A_{ij}	A_{ji}
37.0	1.171	0.863	1.314	0.776	1.117	0.895
88.0	1.184	0.855	1.346	0.763	1.129	0.887
133.0	1.206	0.824	1.371	0.754	1.127	0.886
188.0	1.211	0.840	1.407	0.741	1.150	0.874
237.0	1.223	0.833	1.432	0.732	1.158	0.869

a) MMA=monomethylamine, DMA=dimethylamine, TMA=trimethylamine.

for a given pair of gas molecules i and j, $A_{ij}>A_{ji}$. It has been shown[23] that for a given pair of gas molecules, A_{ij} depends on the ratio $(\sigma_i/\sigma_j)^2$ and on a power less than unity of the mass ratio. For all the cases studied in this work, as may be noted, $\sigma_i>\sigma_j$ and $M_i>M_j$.

The thermal conductivity coefficients of the multi-component mixtures are presented in Tables 7, 8, and 9. As may be seen, the agreement between the theories and the experiment is generally quite good and is

23) T. G. Cowling, P. Gray, and P. G. Wright, *Proc. Roy. Soc. Ser., A*, **276**, 69 (1963).

TABLE 7. THERMAL CONDUCTIVITY COEFFICIENTS OF BINARY MIXTURES OF METHYLAMINES,[a] λ IN UNITS OF cal km^{-1} s^{-1} deg (°C)$^{-1}$

Temp (°C)	Mole[b] fraction	MMA–DMA			MMA–TMA			DMA–TMA		
		λ (exptl)	λ (HE)[c]	λ (Wass)[d]	λ (exptl)	λ (HE)[c]	λ (Wass)[d]	λ (exptl)	λ (HE)[c]	λ (Wass)[d]
37.0	0.25	3.63	3.59	3.60	3.49	3.44	3.49	3.45	3.50	3.47
	0.50	3.66	3.63	3.63	3.53	3.48	3.54	3.49	3.57	3.50
	0.75	3.68	3.67	3.67	3.65	3.56	3.62	3.52	3.64	3.54
88.0	0.25	5.34	5.44	5.36	5.11	5.12	5.07	5.06	5.03	5.03
	0.50	5.38	5.55	5.43	5.31	5.30	5.21	5.18	5.12	5.12
	0.75	5.52	5.61	5.51	5.46	5.40	5.38	5.24	5.20	5.21
133.0	0.25	7.02	6.87	6.93	6.76	6.49	6.54	6.60	6.57	6.50
	0.50	7.09	6.94	7.02	7.01	6.64	6.72	6.76	6.71	6.61
	0.75	7.24	7.07	7.14	7.15	6.89	6.97	7.04	6.81	6.72
188.0	0.25	9.16	8.86	8.82	8.76	8.23	8.30	8.69	8.27	8.24
	0.50	9.18	9.01	8.96	9.04	8.43	8.55	8.89	8.42	8.38
	0.75	9.25	9.02	9.13	9.21	8.77	8.88	9.02	8.56	8.53
237.0	0.25	11.07	10.79	10.81	10.30	10.03	10.04	10.30	10.02	9.98
	0.50	11.18	10.96	10.99	10.52	10.35	10.38	10.35	10.24	10.18
	0.75	11.30	11.19	11.21	10.97	10.81	10.84	10.67	10.45	10.41

a) MMA=monomethylamine, DMA=dimethylamine, TMA=trimethylamine.
b) Mole fraction of the lighter compound.
c) Calculated by the Hirschfelder-Eucken equation.
d) Calculated by the Wassiljewa expression.

TABLE 8. THERMAL CONDUCTIVITY COEFFICIENTS OF TERNARY MIXTURES OF METHYLAMINES[a] AT 37 °C AND AT 88 °C, λ IN UNITS OF cal km^{-1} s^{-1} deg (°C)$^{-1}$

Temp (°C)	Mole fraction			λ(exptl)	λ(HE)[b]	λ(Wass)[c]
	MMA	DMA	TMA			
37.0	0.33	0.33	0.34	3.54	3.52	3.55
	0.17	0.33	0.50	3.51	3.49	3.51
	0.33	0.17	0.50	3.49	3.48	3.53
	0.17	0.50	0.33	3.51	3.52	3.54
	0.33	0.50	0.17	3.60	3.56	3.58
	0.50	0.17	0.33	3.61	3.53	3.57
	0.50	0.33	0.17	3.66	3.57	3.60
88.0	0.33	0.33	0.34	5.20	5.32	4.96
	0.17	0.34	0.49	5.15	5.19	5.01
	0.33	0.18	0.49	5.13	5.23	5.02
	0.17	0.50	0.33	5.23	5.36	4.54
	0.33	0.51	0.16	5.31	5.40	4.62
	0.50	0.32	0.18	5.27	5.45	4.70
	0.46	0.21	0.33	5.24	5.36	5.25

a) MMA=monomethylamine, DMA=dimethylamine, TMA=trimethylamine.
b) Calculated by the Hirschfelder-Eucken equation.
c) Calculated by the Wassiljewa expression.

TABLE 9. THERMAL CONDUCTIVITY COEFFICIENTS OF TWO QUATERNARY MIXTURES OF METHYLAMINES[a] AND AMMONIA AT 37 °C; IN UNITS OF cal km^{-1} s^{-1} deg (°C)$^{-1}$

Mole fraction				λ (exptl)	λ (HE)[b]
NH_3	MMA	DMA	TMA		
0.50	0.17	0.17	0.16	4.30	4.49
0.23	0.27	0.25	0.25	3.70	3.93

a) MMA=monomethylamine, DMA=dimethylamine, TMA=trimethylamine.
b) Calculated by the Hirschfelder-Eucken equation.

within the range of the experimental uncertainties of the measurements (2%). At the higher temperatures, however, the Hirschfelder-Eucken method seems to be the superior one.

It may be mentioned, finally, that we could have arrived at a much better agreement between the experiment and the Wassiljewa extimations by treating the Wassiljewa coefficients as adjustable parameters. This may be done by employing the experimental quantities in the Wassiljewa expression and then carrying out a full computer search to find the "best" pairs of A_{ij}'s. However, more experimental data on the thermal conductivities of the gas mixtures would be needed in order to make a thorough evaluation of such a treatment.

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