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Experimental Data and Procedures for Predicting Thermal Conductivity of Multicomponent Mixtures of Nonpolar Gases

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A hot-wire cell is used to determine the thermal conductivity of Ne, Ar, Kr, Xe, N_2, O_2, H_2, and D_2 gases at 40°, 65°, and 93° C. At these temperatures, the thermal conductivity is also measured as a function of composition for the systems H_2–N_2, H_2–O_2, N_2–O_2, D_2–N_2, H_2–O_2–Ne, H_2–N_2–O_2, H_2–Ar–Kr–Xe, and H_2–D_2–N_2–Ar. These data are compared with the predictions of the theory due to Hirschfelder, procedures due to Mason and Saxena, Lindsay and Bromley, Mathur and Saxena, and Ulybin, Bugrov, and Il'in, and a few simple methods. These detailed calculations and their interpretation in the light of experimental data lend valuable information concerning the status of the art of predicting thermal conductivity of multicomponent mixtures. The thermal conductivity data on binary systems are employed in conjunction with kinetic theory to obtain diffusion and viscosity coefficients.

A NUMBER OF METHODS have been developed for measuring the thermal conductivity of gases and gaseous mixtures [Saxena (*29*), Saxena and Gandhi (*32*)]. The choice of a particular method depends primarily upon environmental conditions (temperature and pressure) of the test gas, and the accuracy desired in the measurement. There is a considerable engineering interest in the thermal conductivity of multicomponent mixtures involving monatomic and polyatomic gases. Further, because it is impossible to have data for all possible choices, it is useful to have a scheme to achieve this goal. We have consequently measured the thermal conductivity of the binary systems H_2–N_2, H_2–O_2, N_2–O_2, and D_2–N_2; the ternary systems H_2–O_2–Ne and H_2–N_2–O_2; and the quaternary systems H_2–Ar–Kr–Xe and H_2–D_2–N_2–Ar. The thermal conductivity of the related eight pure gases was also measured. The measurements were made at 40°, 65°, and 93° C., at a pressure less than 1 atm., and in the case of mixtures as a function of composition. Several almost equally good methods can be adopted for measurement under these conditions.

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The hot-wire method, which we used, has two variants, the thick and the thin wire. In the former, the diameter of the wire is such that the error arising because of the accommodation effect is negligible, but the thermal energy lost from the ends of the wire is appreciable compared to that conducted through the test gas. The end conduction, however, is calculable with good accuracy. In the thin hot-wire cell, on the other hand, accommodation effect is present and is corrected experimentally on the basis of an approximate theory, but the thermal conduction from the two ends is small. We have made an optimum choice for the wire diameter, so that the temperature jump effect is negligible (*12*) and the end conduction loss is small. It is thus possible to keep the magnitude of different corrections small, and obtain accurate absolute values of thermal conductivity.

The experimental data on mixtures are compared with the values obtained by a number of procedures commonly used for the calculation and prediction of thermal conductivity of multicomponent gas mixtures. In particular, we have considered the theoretical expression of Hirschfelder (*15*), and methods which are due to Mason and Saxena (*21*), Lindsay and Bromley (*18*), Mathur and Saxena (*22*), and Ulybin, Bugrov, and Il'in (*41*). The validity of simple procedures such as linear mixing, reciprocal mixing, a combination of the two, and a quadratic expression method is also examined in relation to the new data reported here. This and some previous similar studies are pooled to arrive at useful conclusions for the calculation of thermal conductivity of mixtures of gases. The data on the four binary systems are employed in conjunction with theory to generate the values of two other elementary transport coefficients—viscosity and diffusion.

EXPERIMENTAL

The purities of the gases used in the measurements either singly or in different combinations are given in Table I, with the names of suppliers. Similar information for the platinum wire used in the fabrication of the conductivity cell is included. The complete experimental arrangement consisted of many independent units, such as a high vacuum pumping plant, gas-handling and mixing unit, conductivity cell immersed in a temperature-controlled thermostat, gas compression unit, and electrical measuring system. This has been described by Gambhir *et al.* (*2*).

The pumping system included a two-stage rotary pump, a three-stage mercury diffusion pump, a mercury Mcleod gage, an efficient trap, etc., and could evacuate to a pressure less than 10^{-6} cm. of mercury. The gas mixtures were accurately prepared in a gas-mixing unit (*3*), which was essentially a jacketed buret into which the desired gases were pushed after withdrawing them successively into a pipet from the gas cylinders. The gas transfer was complete and thus the problem of back-diffusion was avoided. The gas mixture was left overnight in the buret and its composition was determined with an accuracy of ±0.01% by measuring the volumes at a constant temperature and known pressure.

The thermal conductivity cell was fabricated (*12*) using a precisely bored stainless steel tube of an effective length of 10.44 cm. and an internal diameter of 0.641_2 cm. The measurements made at various depths showed that the bore was uniform within 1 part in 600. Along the axis of the tube was run a platinum wire 0.0507_6 cm. in diameter. The top end was closed by silver-soldering a brass cap and the bottom end by soldering a Kovar cap through a C-40 glass seal. This design provided the necessary electrical insulation between the cell metal tube and the axial platinum wire. The current and potential leads were soldered at the two metal end caps, while a side tube enabled the cell to be either evacuated or loaded with the test sample. The conductivity cell was mounted vertically in a thermostat bath filled with transformer oil having a flash temperature of about 150° C. Efficient stirring, a distributed immersion heater fed by a regulated power pack, a Jumo contact thermometer along with its sensitive relay system, and a proportional control system made it possible to regulate temperature within ±0.01° C., in the range from room temperature to 100° C. A simple mercury lift system enabled the gas pressure in the conductivity cell to be compressed to different pressure levels. An electrical circuit consisting of the conductivity cell, standard known resistance, etc., was formed and the electrical voltages were measured by a Tinsley vernier potentiometer reading up to 0.1 μv.

After the thermostat bath had acquired the desired temperature, the test sample was introduced into the conductivity cell and left for 2 to 4 hours at the pressure of measurement to stabilize the system thermally. The electrical measurements were taken only after no fluctuations in the potentiometer could be detected over about half an hour. On a test sample at a fixed temperature and pressure electrical measurements were continuously taken six to ten times, but in most cases the differences, if any, were of little consequence in determining the thermal conductivity. The measurement on the same mixture was not repeated at a later time as a separate run, but repeated work on pure gases showed a reproducibility of better than 0.5%. This precision must be regarded as consistent with the compounded uncertainty of the multiple operations involved in a single conductivity measurement.

Earlier detailed experimentation (*12*) with this thick

Table I. Purity Levels of Materials

Material	Purity Specification	Supplier
Neon	Spectral grade	British Oxygen Co., England
Argon	Spectral grade	British Oxygen Co., England
Krypton	99 to 100%, rest xenon	British Oxygen Co., England
Xenon	99 to 100%, rest krypton	British Oxygen Co., England
Nitrogen	99.95%	British Oxygen Co., England
Hydrogen	99.95%	British Oxygen Co., England
Oxygen	99.95%	British Oxygen Co., England
Deuterium	98.6%, rest 0.8% H_2, and 0.6% water vapor	Bhabha Atomic Research Center, Bombay
Platinum wire	99.99%	Ravindra Heraeus & Co., Bombay

hot-wire conductivity cell had indicated that the temperature jump effect was absent for gas pressures above 8 cm. of mercury. Further, the convection effect was not detected (*12*) for gas pressures up to 50 cm. of mercury. Most of our measurements were taken for gas pressures varying between 15 and 20 cm. of mercury. As the thermal conductivity of nondissociating gases is independent of pressure over a range according to theory (*16*), our measured conductivity values may be regarded as appropriate for a pressure of 1 atm. The theory of Kannuluik and Martin (*17*) was used to compute thermal conductivity from the raw experimental data. These were then corrected for the nonradial heat flow at the ends, radiation, and wall effect. The maximum correction due to nonradial heat flow is for hydrogen, about 1.2%, and is almost negligible for krypton and xenon. The radiation correction was determined experimentally (*2*) by taking electrical measurements in vacuum and obtaining from the literature the temperature dependence of the thermal conductivity of platinum. At the highest temperature (93° C.) this correction is least for hydrogen (0.3%) and maximum for xenon (6%). The wall effect correction is calculated theoretically and is very small for our metal cell (0.02%). The error arising from any nonaxiality of the hot wire can be appreciable, about 1% for a wire displacement of 0.05 cm. from the true axis.

Repeated checks on the thermal conductivity of rare gases (*2, 3, 9, 26*) revealed that the cell has no appreciable nonaxial displacement. It is thus clear that the absolute measurement of thermal conductivity is not easy and the magnitude of uncertainty is dependent to some extent upon the value of the conductivity itself. A detailed error analysis revealed that in the most unfavorable case, in which all the errors were assumed to contribute in the same direction, a gas thermal conductivity value within 2% of the true value is obtained, if no error is made in determining the thermal conductivity of the wire. If the gas is pumped out so that the electrical heat generated can flow only along the wire (neglecting radiation), an uncertainty of nearly 1% at most will exist in the conductivity of the wire. The resulting uncertainty in gas conductivity could be then as much as 4%. However, this represents the most unfavorable case, in which all the errors are assumed to contribute in the same direction. On the average, a considerable cancellation of such uncertainties will occur, so that one can expect a much better accuracy. We regard our conductivity values as absolute and estimate a varying uncertainty of 1 to 2%.

The thermal conductivity is measured under a temperature gradient. In our case the platinum wire is several degrees (approximately 5° C.) above the temperature of the outer wall of the conductivity cell, which is the same as the temperature of the thermostat. The measured thermal conductivity is assigned the mean of the hot and cold wall temperatures. This procedure does not lead to appreciable uncertainty, as the temperature difference is rather small. In a few cases we measured the thermal conductivity as a function of the temperature difference between the hot and cold walls and subsequently determined the value of conductivity at the cold wall by extrapolating the plot of conductivity *vs.* temperature difference to the zero value of the latter. Unfortunately, this extrapolation is not easy, because as the temperature difference between the hot and cold walls decreases the uncertainty in the measured conductivity value increases. Further, to decrease the temperature difference below about 2° C. is not practical in our present arrangement. Within all these almost unavoidable limitations, we found that the above-mentioned procedure of temperature assignment involves little avoidable uncertainty. In particular, our experiments at six temperature levels for pure neon, nitrogen, and oxygen indicated that the conductivity values so determined differed from the adopted approach mentioned above by from 1 to 2%. Incidentally, the above experiments reconfirmed the absence of convection in our conductivity cell within the limits of our precision.

The thermal conductivity values as determined from the observed data and after the application of necessary corrections are reported in Tables II, III, IV, and V for pure gases and binary, ternary, and quaternary mixtures, respectively. In each case—*i.e.*, a pure gas or a particular mixture of fixed composition—the directly measured conductivity values were plotted as a function of temperature and read at 40°, 65°, and 93° C., temperatures at which the thermostat bath was actually operated. The mixture compositions as reported in these tables correspond to the experimental test gas mixtures. We also neglect any separation of the mixture because of thermal diffusion. This is mostly justified because of the smallness of such a separation in the absolute sense, and the small temperature difference between the hot

Table II. Comparison of Measured Thermal Conductivity Values (μWm.$^{-1}$ Deg.$^{-1}$) with Literature and Theoretical Values

	Gas								
Temp., ° C.	Ne	Ar	Kr	Xe	N_2	O_2	H_2	D_2	
40	0.0496	0.0185	0.00984	0.00593	0.0268	0.0281	0.182	0.135	Present
	0.0502	0.0185	0.00988	0.00619	0.0268	0.0278	0.185	0.137	Literature
	(+1.3)	(0.0)	(+0.4)	(+4.4)	(0.0)	(−1.1)	(+1.6)	(+1.5)	% dev.
	0.0501	0.0183	0.00980	0.00588	0.0277	0.0280	0.192	0.136	Theoretical
	(+1.0)	(−1.1)	(−0.4)	(−0.9)	(+3.4)	(−0.4)	(+5.5)	(+1.0)	% dev.
65	0.0534	0.0193	0.0108	0.00619	0.0290	0.0291	0.194	0.143	Present
	0.0532	0.0196	0.0106	0.00661	0.0283	0.0296	0.198	0.143	Literature
	(−0.4)	(+1.5)	(−1.8)	(+6.9)	(−2.4)	(+1.7)	(+2.1)	(0.0)	% dev.
	0.0528	0.0195	0.0105	0.00652	0.0294	0.0298	0.202	0.144	Theoretical
	(−1.1)	(+1.1)	(−2.3)	(+5.3)	(+1.4)	(+2.4)	(+4.1)	(+0.7)	% dev.
93	0.0563	0.0210	0.0114	0.00706	0.0312	0.0313	0.204	0.149	Present
	0.0561	0.0209	0.0114	0.00707	0.0301	0.0318	0.209	0.152	Literature
	(−0.3)	(−0.5)	(0.0)	(+0.2)	(−3.5)	(+1.6)	(+2.5)	(+2.0)	% dev.
	0.0557	0.0208	0.0113	0.00703	0.0312	0.0317	0.214	0.152	Theoretical
	(−1.0)	(−1.0)	(−0.9)	(−0.5)	(0.0)	(+1.2)	(+5.0)	(+2.0)	% dev.

wire and the cold wall of the conductivity cell makes it even smaller in our case.

CALCULATIONS

In Table II we compare our measured thermal conductivity values with those obtained by a critical evaluation of literature data (*8, 35*). In general, the agreement between the two sets is very satisfactory and this confirms the absolute nature of our measurements and our experimental accuracy. This comparison is of great relevance for multicomponent mixtures where similar measurements are not available for direct comparison. The theoretically calculated values are also given in

Table III. Experimental and Calculated Thermal Conductivity Values for Binary Mixtures

Gas Pair	x_i[a]	Exptl., μWm.$^{-1}$ Deg.$^{-1}$	Hirschfelder	Mason and Saxena	Lindsay and Bromley	Mathur and Saxena	Ulybin *et al.*
H_2-N_2							
40° C.	0.147	0.1414	+2.9	+2.4	−0.8	+2.0	. . .
	0.338	0.1027	+0.5	+3.6	−1.7	+2.9	. . .
	0.592	0.0677	−3.4	+1.0	−4.8	. . .	. . .
65° C.	0.147	0.1496	+2.7	+3.1	−0.2	+2.7	+0.9
	0.338	0.1078	+1.2	+5.2	−0.2	+4.5	+2.0
	0.592	0.0715	−3.0	+2.3	−3.5	+1.5	+1.8
93° C.	0.147	0.1590	+2.3	+2.1	−1.2	+1.7	+0.3
	0.338	0.1161	−0.4	+3.1	−2.3	+2.4	+0.4
	0.592	0.0766	−4.0	+1.2	−4.6	+0.4	+1.3
H_2-O_2							
40° C.	0.209	0.1280	+2.9	+4.5	+0.3	+1.4	. . .
	0.491	0.0812	−1.0	+4.7	−1.2	. . .	. . .
	0.796	0.0451	−0.3	+5.0	+0.6	+1.3	. . .
65° C.	0.209	0.1377	+1.4	+3.1	−1.0	0.0	−1.5
	0.491	0.0868	−1.7	+3.4	−2.4	−1.3	−1.7
	0.796	0.0489	−2.2	+1.5	−2.9	−2.2	−3.9
93° C.	0.209	0.1456	+1.3	+2.7	−1.4	−0.4	−1.6
	0.491	0.0928	−2.8	+2.3	−3.5	−2.3	−2.3
	0.796	0.0527	−3.8	+0.3	−4.0	−3.3	−4.6
N_2-O_2							
40° C.	0.249	0.0272	+2.7	−2.5	−0.4	−1.1	. . .
	0.529	0.0271	+2.9	−1.8	+1.4	. . .	. . .
	0.762	0.0272	+2.9	0.0	+2.2	+1.2	. . .
65° C.	0.249	0.0291	+1.4	−2.6	−0.3	−1.3	0.0
	0.529	0.0291	+1.8	−3.4	−0.3	−1.6	−1.5
	0.762	0.0295	+0.6	−4.0	−1.7	−2.7	−3.5
93° C.	0.249	0.0313	0.0	−2.4	0.0	−1.1	+0.1
	0.529	0.0313	+0.6	−3.2	0.0	−1.4	−1.5
	0.762	0.0310	+1.9	−1.3	+1.0	0.0	−1.2
D_2-N_2							
40° C.	0.222	0.0938	+0.7	+4.1	+3.1	+3.7	. . .
	0.601	0.0550	−4.3	+0.5	−0.8	. . .	. . .
65° C.	0.222	0.1004	−0.8	+2.9	+1.8	+2.5	−0.6
	0.601	0.0578	−3.9	+1.7	+0.4	+1.2	+2.1
93° C.	0.222	0.1063	−1.0	+2.2	+1.1	+1.9	−1.3
	0.601	0.0621	−5.3	+0.3	+1.1	0.0	+1.0

[a] Mole fractions of heavier component in mixture in each case.

Table IV. Experimental and Various Calculated Thermal Conductivity Values for Ternary Mixtures

Gas System	x_1	x_2	Exptl., μWm.$^{-1}$ Deg.$^{-1}$	Hirschfelder	Mason and Saxena	Lindsay and Bromley	Mathur and Saxena	Ulybin *et al.*
H_2-O_2-Ne								
40° C.	0.234	0.135	0.1044	. . .	+6.9	+2.5	+2.4	. . .
	0.655	0.215	0.0437	. . .	−0.3	−1.1	−0.3	. . .
65° C.	0.234	0.135	0.1184	. . .	0.0	−4.0	−4.2	−6.5
	0.655	0.215	0.0447	. . .	+2.4	+1.6	+2.3	+2.5
93° C.	0.234	0.135	0.1180	. . .	+3.5	−1.4	−0.8	−0.9
	0.655	0.215	0.0490	. . .	−0.3	−1.3	−0.4	−0.2
H_2-N_2-O_2								
40° C.	0.296	0.097	0.0946	+0.5	+4.7	−0.6	+1.4	. . .
	0.266	0.535	0.0454	−3.2	−1.2	−4.0	−1.9	. . .
65° C.	0.296	0.097	0.1010	−0.2	+4.6	−1.4	+0.6	−0.9
	0.266	0.535	0.0475	−1.9	+1.0	−2.4	−0.2	+1.9
93° C.	0.296	0.097	0.1083	−1.6	+2.4	−2.9	−0.9	−1.9
	0.266	0.535	0.0509	−3.1	0.0	−3.0	−0.8	+1.8

Table II. The expressions given by Hirschfelder *et al.* (*16*) and Hirschfelder (*15*) for monatomic and polyatomic gases, respectively, are used in conjunction with the exp-six potential parameters in Table VI. The agreement between theory and experiment is satisfactory in all cases except for some of the polyatomic gases. The numbers within parentheses (Table II) are the percentage disagreement between the currently measured values and other experimental or calculated values. Part of the disagreement may be due to the approximate nature of the theory (*15*), as the thermal relaxation of internal energy is neglected. We do not consider the two other theories (*19, 36*), which attempt to correct approximately for the exchange between translational and internal energies.

The experimental data and various calculated results for the thermal conductivity of binary systems are reported in Table III. According to the theory of Hirschfelder (*15*), the thermal conductivity of a multicomponent mixture is given by

$$k_{\text{mix}} = k^\circ_{\text{mix}} + \sum_{i=1}^{n} (k_i - k_i^\circ)\left[1 + \sum_{\substack{j=1\\ j \pm i}}^{n} \frac{D_{ii}}{D_{ij}}\frac{x_j}{x_i}\right]^{-1} \tag{1}$$

The k°_{mix} expression as given by Muckenfuss and Curtiss (*28*) and modified by Mason and Saxena (*20*) is used. The exp-six potential with parameters given in Tables VI and VII is preferred in our calculations. The actual calculated values are not reported, but instead their percentage deviations from the corresponding experimental values. The deviations are consistently designated as positive whenever the calculated values are greater than the experimental results. This procedure renders the assessment of the computed results much more straightforward. The approximate theory of Hirschfelder seems to be remarkably successful. The average absolute deviation for the 33 mixtures is 2.1%.

Table V. Experimental and Various Calculated Thermal Conductivity Values of Quaternary Mixtures

Gas System	x_1	x_2	x_3	Exptl.	Mason and Saxena	Lindsay and Bromley	Mathur and Saxena	Ulybin *et al.*
H_2-Ar-Kr-Xe								
40° C.	0.306	0.102	0.200	0.0469	−1.5	−13.1	−1.6	...
	0.240	0.165	0.453	0.0230	+2.7	− 3.6	+1.2	...
65° C.	0.306	0.102	0.200	0.0499	−1.8	−13.5	−1.9	−0.6
	0.240	0.165	0.453	0.0256	−2.5	− 8.6	−4.0	+1.0
93° C.	0.306	0.102	0.200	0.0538	−3.4	−14.9	−3.5	−3.2
	0.240	0.165	0.453	0.0280	−4.5	−10.4	−5.8	+0.4
H_2-D_2-N_2-Ar								
40° C.	0.152	0.144	0.346	0.0942	+3.6	+ 2.1	−0.8	...
	0.132	0.504	0.158	0.0552	+2.0	− 1.1	+0.2	...
65° C.	0.152	0.144	0.346	0.1010	+2.6	+ 0.6	−1.8	−1.0
	0.132	0.504	0.158	0.0589	+1.9	− 1.1	+0.2	+0.2
93° C.	0.152	0.144	0.346	0.1074	+1.6	− 0.4	−2.7	−1.5
	0.132	0.504	0.158	0.0624	+2.2	− 0.9	+0.3	+1.0

Table VI. Exp-Six Potential Parameters and Sutherland Constants for Pure Gases

Gas	α	ε/k, ° K.	r_m, A.	S
Ne	14.5	38.0	3.147	61
Ar	14.0	123.2	3.866	147
Kr	13.5	200	4.036	188
Xe	13.0	231.2	4.450	252
N_2	17.0	101.2	4.011	102.7
O_2	17.0	132	3.726	138
H_2	14.0	37.3	3.337	83
D_2	14.0	37.3	3.337	83

Table VII. Exp-Six Potential Parameters and Sutherland Constants for Binary Gas Systems

Gas Pair	α_{12}	ε_{12}/k,° K.	$(r_m)_{12}$, A.	S_{12}
H_2-N_2	15.6	59.0	3.690	92.4
H_2-O_2	15.6	67.9	3.551	107
N_2-O_2	17.0	116	3.861	119
D_2-N_2	15.6	59	3.690	92.4

According to Mason and Saxena (*21*), the thermal conductivity of a multicomponent mixture is given by

$$k_{\text{mix}} = \sum_{i=1}^{n} k_i\left[1 + \sum_{\substack{j=1\\ j \pm i}}^{n} \phi_{ij}\frac{x_j}{x_i}\right]^{-1} \tag{2}$$

where

$$\phi_{ij} = \frac{1.065}{2(2)^{\frac{1}{2}}}\left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}}\left[1 + \left(\frac{k_i^\circ}{k_j^\circ}\right)^{\frac{1}{2}}\left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2 \tag{3}$$

This expression is derived from Equation 1 by making well defined approximations (*21*). The computed values of constants ϕ_{ij} for the four binary systems at 40° C. are given in Table VIII and are used at 65° and 93° C. ϕ_{ij} are known to depend very feebly on temperature (*6, 22*) and consequently this procedure is justified. The deviations of the calculated conductivities from the experimental values are given in column 5 of Table III; the average absolute deviation for all the mixtures is 2.6%.

Lindsay and Bromley (*18*) derived an expression for thermal conductivity coefficient similar to Equation 2, except that ϕ_{ij} are now defined as follows:

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

The Sutherland constants for the pure gases are given by Chapman and Cowling (*1*) and reproduced in Table VI. These constants for the binary systems were generated by the geometric mean rule (Table VII). The

Table VIII. Values of ϕ_{ij} at 40° C.

Gas Pair	Mason and Saxena		Lindsay and Bromley		Mathur and Saxena	
	ϕ_{12}	ϕ_{21}	ϕ_{12}	ϕ_{21}	ϕ_{12}	ϕ_{21}
H_2-N_2	0.293	2.035	0.578	2.081	0.297	2.064
H_2-O_2	0.285	1.946	0.578	1.980	0.310	2.116
N_2-O_2	1.074	1.055	1.025	0.974	1.036	1.017
D_2-N_2	0.401	1.970	0.616	1.863	0.404	1.987

method predicts the directly observed values of thermal conductivity of Table III, within an average absolute deviation of 1.6%. The related ϕ_{ij} at 40° C. are given in Table VIII.

Mathur and Saxena (*22*) showed on the basis of Equation 3 that

$$\frac{\phi_{ij}}{\phi_{ji}} = \frac{M_j}{M_i}\frac{\eta_i}{\eta_j} \tag{5}$$

Thus, if one value of mixture thermal conductivity is known, Relations 2 and 5 can be used to compute ϕ_{ij} and ϕ_{ji}. For the four binary systems examined here we find the ϕ_{ij} values given in Table VIII. The calculated values of thermal conductivity for the 29 mixtures of Table III agree with the directly observed values within an average absolute deviation of 1.7%.

Ulybin *et al.* (*41*) suggested an empirical procedure for computing the thermal conductivity of a mixture at a higher temperature from the known thermal conductivity of the mixture at some lower temperature and also of all the related pure components at these two temperatures. Thus,

$$k_{\text{mix}}(T_2) = k_{\text{mix}}(T_1) \sum_{i=1}^{n} x_i \frac{k_i(T_2)}{k_i(T_1)} \tag{6}$$

Here temperature T_2 is greater than T_1. A check of this suggested procedure is possible on the basis of thermal conductivity data presented here. In each case 40° C. data are used and k_{mix} at 65° and 93° C. are computed. The agreement with the directly observed values is indicated in the last column of Table III. The average absolute deviation is 1.6% for 22 mixtures.

The calculated values according to the various methods for the ternary mixtures are compared against the directly measured values in Table IV. The rigorous calculations for six mixtures of hydrogen-nitrogen-oxygen essentally confirm the adequacy of the theory for multicomponent mixtures. The success of the other computing procedures is about the same as for binary systems. The procedures of Mason and Saxena, Lindsay and Bromley, Mathur and Saxena, and Ulybin *et al.* reproduce the experimental data on 12 ternary mixtures within average absolute deviations of 2.3, 2.2, 1.4, and 2.1%, respectively. A similar study for two quaternary systems and 12 of their mixtures is presented in Table V. The methods of Mason and Saxena, Lindsay and Bromley, Mathur and Saxena, and Ulybin *et al.* correlate the observed conductivity values with an average absolute deviation of 2.5, 6.0, 2.0, and 1.1%, respectively. Other than the Lindsay and Bromley method, here again all the computing procedures are about the same in reproducing the observed values as in the case of binary and ternary systems.

The procedure of Ulybin *et al.* (*41*) is entirely empirical in nature, but Equation 6 reduces to Equation 2 (Wassiljewa form) if ϕ_{ij} are assumed to be independent of temperature and the same value for the temperature coefficient of thermal conductivity is assigned for all the pure gases of the mixture. Thus, all four methods (*18, 21, 22, 41*) are based on the Wassiljewa relation. The methods due to Mason and Saxena (*21*) and Lindsay and Bromley (*18*) involve explicit expressions for the Wassiljewa coefficients, ϕ_{ij}. Further, in the first method (*21*) the ϕ_{ij} are written in terms of k_i° (or η_i) and there is no other adjustable constant. The method of Lindsay and Bromley (*18*) on the other hand requires S_i in addition to η_i and this limits the general applicability of the method but increases its accuracy in many cases, because of better adjustment now possible than in the method of Mason and Saxena (*21*). The method of Mathur and Saxena (*22*) requires one k_{mix} value at any composition, but that of Ulybin *et al.* (*41*) requires this value to be for the same composition as the unknown mixture. This requirement is not easy to fulfill and becomes increasingly difficult as the number of components in the mixture increases. These numerical calculations indicate that the four methods are almost equally successful in reproducing the present data on binary, ternary, and quaternary systems, and the method of Mathur and Saxena (*22*) appears attractive from the viewpoints of simplicity, accuracy, and the amount of initial information needed. It would be very convenient if a simple but reliable procedure could be found for computing k_{mix}, wherein the conductivity values for the related binary combinations were not needed.

Many simpler procedures have been used for the thermal conductivity of mixtures of rare (*7, 26, 30*) and polyatomic gases (*11*).

SIMPLE MIXING RULE.

$$k_{\text{mix}} = \sum_{i=1}^{n} x_i k_i \tag{7}$$

RECIPROCAL MIXING RULE.

$$k_{\text{mix}}^{-1} = \sum_{i=1}^{n} (x_i/k_i) \tag{8}$$

COMBINATION OF TWO PROCEDURES.

$$k_{\text{mix}} = 0.5\left[\sum_{i=1}^{n} x_i k_i + \frac{1}{\sum_{i=1}^{n} (x_i/k_i)}\right] \tag{9}$$

QUADRATIC EXPRESSION METHOD.

$$k_{\text{mix}} = x_1^2 k_1 + x_1 x_2 k_{12} + x_2^2 k_2 \tag{10}$$

k_{12} is an empirical constant, determined from one known value of k_{mix}.

The results of the numerical calculation for the four binary systems and the four procedures outlined above are given in Table IX. They are in general agreement with what is obtained in most of the previous calculations (*7, 11, 26, 30*) of this nature. The simple and reciprocal mixing rules over- and underestimate the conductivity values, respectively, but the combination of the two leads to fair estimates, though not as accurately as the method of Mathur and Saxena (*22*). The quadratic expression method is not very encouraging and is included here more because of its historical importance as one of the early forms used for representation and correlation of k_{mix} data.

DIFFUSION AND VISCOSITY COEFFICIENTS

Within the framework of general kinetic theory interconnecting relations among different transport coefficients have been developed, which are essentially independent of the detailed nature of the intermolecular force laws, except that these must be central. Further, such relations in general involve only measurable quantities, so that if all the related experimental information is available, new transport property data can be generated on the basis of data on another transport property. Here we adopt this approach and generate coefficients of diffusion and viscosity for binary systems utilizing the experimental data of thermal conductivity of Tables II and III.

Gandhi and Saxena (*10*) and Mathur and Saxena (*24*) have developed and checked the interrelations between thermal conductivity and diffusion coefficients for pure gases and mixtures of monatomic as well as polyatomic gases. The pertinent relations are briefly reproduced below. The starting equation for the computation of D_{ij} is 1, wherein

$$k^\circ_{\text{mix}} = \frac{4\,(x_1^2L_{22} - 2x_1x_2L_{12} + x_2^2L_{11})}{(L_{12}^2 - L_{11}L_{22})} \qquad (11)$$

$$L_{11} = -\frac{4x_1^2}{k_1^\circ} - \frac{16T}{25p}\,\frac{x_1x_2}{D_{12}}\,\frac{(15/2)M_1^2 + (59/20)M_2^2 + (22/5)M_1M_2}{(M_1 + M_2)^2} \qquad (12)$$

$$L_{12} = \frac{484}{125}\,\frac{Tx_1x_2}{pD_{12}}\,\frac{M_1M_2}{(M_1 + M_2)^2} \qquad (13)$$

$$k_i^\circ = k\left[0.115 + 0.354\,\frac{\gamma}{\gamma - 1}\right]^{-1} \qquad (14)$$

and

$$D_{11} = \frac{8.8Tk_1}{25p}\left[0.115 + 0.354\,\frac{\gamma}{\gamma - 1}\right]^{-1} \qquad (15)$$

Table IX. Experimental and Calculated k_{mix} Values According to Simpler Procedures for Binary Systems

Gas Pair	X_i	Eq. 7	Eq. 8	Eq. 9	Eq. 10
H_2-N_2					
40° C.	0.147	+12.7	−30.4	−8.9	+ 2.0
	0.338	+26.3	−40.0	−6.8	. . .
	0.592	+33.2	−39.2	−3.0	− 9.8
65° C.	0.147	+13.3	−29.4	+0.3	+ 2.0
	0.338	+28.1	−38.4	−5.2	. . .
	0.592	+34.6	−37.9	−1.6	−11.1
93° C.	0.147	+12.2	−29.3	−8.6	+ 1.8
	0.338	+25.2	−38.8	−6.8	. . .
	0.592	+32.1	−37.7	−2.5	− 8.6
H_2-O_2					
40° C.	0.209	+17.2	−33.7	−8.2	+ 4.1
	0.491	+31.3	−39.2	−4.0	. . .
	0.796	+31.9	−24.7	+3.6	− 4.5
65° C.	0.209	+15.7	−35.6	−9.9	+ 3.3
	0.491	+30.0	−41.1	−5.5	. . .
	0.796	+28.1	−28.1	0.0	− 6.5
93° C.	0.209	+15.2	−34.9	−9.9	+ 3.2
	0.491	+28.2	−40.7	−6.2	. . .
	0.796	+25.3	−28.2	−1.0	− 6.2
N_2-O_2					
40° C.	0.249	− 0.3	− 0.3	−0.3	− 1.1
	0.529	+ 1.4	+ 1.4	+1.4	. . .
	0.762	+ 2.2	+ 2.2	+2.2	+ 1.2
65° C.	0.249	− 0.3	− 0.3	−0.3	0.0
	0.529	− 0.3	− 0.3	−0.3	. . .
	0.762	− 1.7	− 1.7	−1.7	− 1.5
93° C.	0.249	0.0	0.0	0.0	0.01
	0.529	0.0	0.0	0.0	. . .
	0.762	+ 1.0	+ 1.0	+1.0	+ 1.2
D_2-N_2					
40° C.	0.222	+18.3	−24.0	−2.8	. . .
	0.601	+27.3	−28.3	−0.5	−16.1
65° C.	0.222	+16.8	−24.1	−3.6	. . .
	0.601	+28.4	−26.5	+1.0	−12.2
93° C.	0.222	+15.9	−23.6	−3.9	. . .
	0.601	+26.2	−26.5	−0.2	−11.5

Expressions for L_{22}, $k_2°$, and D_{22} are obtained from L_{11}, $k_1°$, and D_{11} by interchanging subscripts 1 and 2. $k°_{mix}$ is obtained from Equations 11, 12, and 13 in terms of pD_{12}; $k_i°$ and pD_{ii} are readily obtained from the known values of k_i using Equations 14 and 15, respectively, and hence D_{12} from Equation 1. In practice an iterative method was found easier, where a guessed value of D_{12} was used to evaluate the right side of Equation 1 and the whole procedure was repeated with another choice of D_{12} until the computed value of k_{mix} agreed well with its experimental value. The diffusion coefficient is calculated for each composition of the mixture (column 3 of Table X), but the present procedure is not sensitive enough to bring out the feeble composition dependence of the diffusion coefficient with enough accuracy. We have consequently averaged the values referring to different compositions and list these mean values in column 4. The values of the diffusion coefficient graphically interpolated from those available in the literature are reproduced in column 5, and the theoretically computed values (*16*) on the exp-six potential (Table VII) in column 6. The three sets of diffusion coefficients are in fair agreement with each other and give an approximate estimate of the accuracy of this indirect approach.

Saxena and Agrawal (*31*) described the relation connecting thermal conductivity and viscosity of binary gas mixtures and demonstrated its reliability by performing calculations on rare gas mixtures. The working relations are as follows:

$$\eta_{mix} = \frac{x_1^2H_{22} - 2x_1x_2H_{12} + x_2^2H_{11}}{H_{11}H_{22} - H_{12}^2} \tag{16}$$

$$H_{11} = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2}{(M_1 + M_2)}\frac{RT}{pD_{12}}\left[1 + \frac{3.30M_2}{5M_1}\right] \tag{17}$$

$$H_{12} = -\frac{0.68x_1x_2RT}{(M_1 + M_2)pD_{12}} \tag{18}$$

and

$$\eta_i = \frac{4M}{15R}k_i° \tag{19}$$

Table X. Indirectly Generated Coefficients of Diffusion, D_{ij}, (Sq. μM/s) at 1 Atm. and Viscosity, η_{mix}, (μNs/Sq. M.) for Binary Systems

Gas Pair	X_1	D_{ij} Generated	Mean	Measured	Theoretical	Generated η_{mix}
H_2–N_2						
40° C.	0.147	90.6				13.6
	0.338	91.3	92.6	85.0[a]	82.8	16.4
	0.592	95.9				17.9
65° C.	0.147	100.6				14.2
	0.338	100.5	102.5	98.0[a]	94.3	17.2
	0.592	106.5				18.8
93° C.	0.147	118.6				15.2
	0.338	119.5	120.7	112.5[a]	107.9	18.3
	0.592	123.9				20.1
H_2–O_2						
40° C.	0.209	91.7				16.0
	0.491	94.9	92.9	88.0[b]	86.5	19.7
	0.796	92.0				21.1
65° C.	0.209	107.8				17.2
	0.491	109.8	109.9	102.0[b]	98.6	21.0
	0.796	112.2				22.4
93° C.	0.209	125.2				18.3
	0.491	128.6	128.6	118.0[b]	112.9	22.5
	0.796	132.1				23.9
N_2–O_2						
40° C.	0.249	22.4				18.9
	0.529	21.7	21.7	22.4[c]	22.3	19.6
	0.762	21.1				20.1
65° C.	0.249	25.7				20.4
	0.529	25.7	26.1	25.6[c]	25.5	21.3
	0.762	26.8				22.0
93° C.	0.249	29.4				21.4
	0.529	29.4	29.1	29.3[c]	29.3	22.3
	0.762	28.6				23.1
D_2–N_2						
40° C.	0.222	61.5				16.3
	0.601	67.7	64.6	. . .	60.5	18.2
65° C.	0.222	72.1				17.2
	0.601	75.4	73.7	. . .	68.9	19.3
93° C.	0.222	83.6				18.3
	0.601	88.1	85.8	. . .	78.8	20.5

[a] (*39*).
[b] (*42*).
[c] (*43*).

Again H_{22} and η_2 are obtained from H_{11} and η_1, respectively, by interchanging subscripts 1 and 2. Values of pD_{12} and k_i° obtained in the previous calculations are used in Equations 17, 18, and 19 and thence η_{mix} values are obtained from Equation 16 and are listed in the last column of Table X. The directly measured viscosity values for the hydrogen-oxygen and nitrogen-oxygen systems agree with the indirectly generated values within an average absolute deviation of 3.0 and 1.0%, respectively. Thus the indirect approach used to compute transport properties is attractive and will invariably lead to numbers adequate for calculations in engineering problems.

CONCLUSIONS

A number of attempts have been made to assess the adequacy of the various computing procedures against the directly measured thermal conductivity values (*3–9, 11, 13, 16, 18, 21, 22, 23, 25, 26, 30, 33, 38, 41*). Others can be traced through these references. It is possible to derive some general guidelines for computing the thermal conductivity of multicomponent mixtures of nonpolar gases by pooling the conclusions drawn in the above-mentioned studies. Tondon and Saxena (*40*) recently checked some of the existing methods and suggested a new one for the calculation of the thermal conductivity of polar and nonpolar gas mixtures.

The theory of Hirschfelder is adequate for approximate estimates of the thermal conductivity of multicomponent mixtures involving polyatomic gases. For many simple polyatomic gases the uncertainty may be about 2 to 5%. The use of more complicated theories (*19, 27, 36, 37*), in the authors' opinion, will be meaningful only after some adequate understanding is developed for the process describing the diffusion of internal energies of polyatomic gases.

The procedures due to Lindsay and Bromley and Mason and Saxena reproduce the experimental data in most cases with an accuracy within about 2 to 3%. The latter method is the simpler of the two and hence preferable for practical reasons.

The methods due to Mathur and Saxena and Ulybin, Bugrov, and Il'in require information as to the thermal conductivity of the mixture also. The requirement in the latter case is more stringent, for the thermal conductivity of the mixture used in the calculation must refer to the same composition as the unknown one at a different temperature. The accuracy of both the methods is about 2%.

The simple methods, Equations 7 through 10, are not attractive for practical use. The method based on Equation 9 is appropriate for quick and crude estimates.

Thermal conductivity data in conjunction with theory are reasonably good in estimating viscosity and diffusion coefficients. The reverse procedure is also used to generate thermal conductivity data with good success (*14*).

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NOMENCLATURE

D_{ii} = self-diffusion coefficient of pure component i, sq. cm./sec.
D_{ij} = binary diffusion coefficient of components i and j, sq. cm./sec.
k_i° = thermal conductivity of the pure component i with frozen internal degrees of freedom, $\text{Wm.}^{-1}\ \text{deg.}^{-1}$
k_i = thermal conductivity of pure component i, $\text{Wm.}^{-1}\ \text{deg.}^{-1}$
k°_{mix} = thermal conductivity of multicomponent mixture with frozen internal degrees of freedom, $\text{Wm.}^{-1}\ \text{deg.}^{-1}$
k_{mix} = thermal conductivity of multicomponent mixture, $\text{Wm.}^{-1}\ \text{deg.}^{-1}$
$k_i(T_1)$ = k_i at T_1
$k_i(T_2)$ = k_i at T_2
$k_{\text{mix}}(T_1)$ = k_{mix} at T_1
$k_{\text{mix}}(T_2)$ = k_{mix} at T_2
M_i or M_j = molecular weight of component i or j
n = total number of components in mixture
p = pressure, atm.
r_m = distance parameter of potential at which latter has minimum value, A.
$(r_m)_{12}$ = unlike molecular interaction, A.
R = gas constant
S_i = Sutherland constant for component i, deg.^{-1}
S_{ij} = Sutherland constant for components i and j, deg.^{-1}
T = temperature, ° K.
x_1 = mole fraction of heaviest component in mixture
x_2 = mole fraction of second heaviest component in mixture
x_3 = mole fraction of third heaviest component in mixture
x_i or x_j = mole fractions of component i or j in mixture

GREEK LETTERS

α = parameter, measure of steepness of repulsive potential
α_{12} = α referring to unlike molecular interaction
γ = ratio of specific heat of a gas at constant pressure to that at constant volume
ε/k = depth of potential energy well divided by Boltzmann constant, k, ° K.
ε_{12}/k = ε/k referring to unlike molecular interaction, ° K.
η_i or η_j = viscosity coefficient of pure component i or j, Ns./sq. m.
η_{mix} = viscosity coefficient of mixture, Ns./s. m.
ϕ_{ij} = constant which depends upon quantities characterizing components i and j of mixture

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Chemical and Isotopic Equilibria Involving Liquid and Gaseous Nitrogen Oxides

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Existing experimental data dealing with liquid-gas-phase equilibria among the oxides of nitrogen (NO, NO_2, N_2O_3, and N_2O_4) have been re-examined, and an improved method has been developed for calculating the gas-phase composition for a given liquid phase and temperature. The method has been used to calculate chemical compositions in such systems over a wide range of temperature and total pressure. The effective single-stage separation factor for concentrating nitrogen-15 by this exchange system has also been evaluated over a broad range of operating conditions.

WHEN A LIQUID MIXTURE of oxides of nitrogen is equilibrated with its vapor, nitrogen-15 preferentially concentrates in the liquid phase. The effective single-stage fractionation factor, α_{eff}, of such an isotope exchange system depends on the temperature and pressure through two factors: The chemical compositions of the two phases depend upon the temperature and pressure; the quantum-mechanical distribution of isotopes among various chemical species is itself a function of temperature. The latter is directly calculable by the method of Bigeleisen and Mayer (*8*).

The exchange system, which consists of a liquid mixture of oxides of nitrogen and its vapor (hereafter referred to as the N_2O_3-NO system), was used by Monse *et al.* (*13, 15*) to prepare samples of highly enriched ^{15}N in an exchange column operated at atmospheric pressure. The effective single-stage separation factor ranged from 1.035 ±0.005 at −14° C. to 1.016 ± 0.004 at +14° C.