Subscripts

A,B,N_2,He = gas components, A, B, N_2, and He

0,1 = conditions at entrance and exit of diffusion paths through the pellet

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Thermal Conductivity of Gas Mixtures

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Thermal conductivities of ten gases and selected binary and ternary mixtures of them were measured in a concentric silver cylinder cell over the temperature range from 100° to 540°C. The gases were helium, argon, nitrogen, oxygen, carbon dioxide, methyl ether, and methyl formate.

Correlations based upon empirical equations derived from kinetic theory have been developed for the thermal conductivity of gas mixtures. For mixtures of polyatomic molecules the energy transport is considered in two parts, that is one portion transferred by collision and the other by diffusion. When compared with the experimental data for 226 binary mixtures over temperatures from 0° to 774°C., the conductivity equation proposed in this work shows an average deviation of 2.1%.

Rigorous methods for calculation of thermal conductivity of mixed gases have been developed by Hirschfelder and associates (*11, 13, 14*) based on the classical Chapman-Cowling approach (5). These methods are rather lengthy and laborious to use. A number of more simple semiempirical methods have been proposed which appear to be reasonably accurate (*2a, 21, 23, 24, 25*).

A new method is proposed in this paper based on an extension of the elementary kinetic theory to mixtures. It is believed that shortcomings in the theory are absorbed to a considerable extent by relating the mixture properties to pure component values. On the basis of new experimental data at elevated temperatures which are also reported here it seems that the method may be particularly useful in predicting the temperature dependence of thermal conductivity for mixtures.

DEVELOPMENT OF THE THERMAL-CONDUCTIVITY CORRELATION

In accordance with the kinetic theory the thermal diffusivity, diffusion coefficient, and kinematic viscosity for an ideal gas are of the order of the product of the mean free path and the root-mean-square velocity of the molecules:

$$\frac{\lambda}{\rho C_v} \approx D \approx \frac{\eta}{\rho} \approx \Lambda v \qquad (1)$$

For a single component system

$$\lambda_1 \approx D_{11} \rho_1 C_{v_1} \qquad (2)$$

Thus thermal conductivity is proportional to the rate of movement of the individual molecules within the gas and to the heat capacity per unit volume of the molecules. Analogously for the same gas in a mixture

$$\lambda_{1m} \approx D_{1m} \rho_{1m} C_{v_1} \qquad (3)$$

Dividing Equation (3) by (2) and assuming the proportionality constant to be the same in both expressions one finds

$$\frac{\lambda_{1m}}{\lambda_1} = \frac{D_{1m} \rho_{1m}}{D_{11}\rho_1} = x_1 \frac{D_{1m}}{D_{11}} \qquad (4)$$

The diffusion coefficient D_{1m} is a measure of the rate of movement of any molecule of Type I within a mixture consisting of Type I and molecules of other types. Following Wilke's treatment of the diffusion of a gas into a multicomponent mixture one may write D_{1m} as (35)

$$\frac{1}{D_{1m}} = \frac{x_1}{D_{11}} + \frac{x_2}{D_{12}} + \ldots \qquad (5)$$

Here x_1 and D_{1m} are included, since self-diffusion of molecules of species 1 having different thermal energies is important in the conduction process. After Equation (5) is multiplied through by D_{11} and inverted, the ratio D_{1m}/D_{11} required in Equation (4) is obtained:

$$\frac{D_{1m}}{D_{11}} = \frac{1}{x_1 + \frac{D_{11}}{D_{12}} x_2 + \frac{D_{11}}{D_{13}} x_3 + \ldots} \qquad (6)$$

The thermal conductivity of a mixture is the sum of the conductivities of the individual components; that is

$$\lambda_c = \lambda_{1m} + \qquad (7)$$

As will be explained below, λ_c is that part of the conductivity of a mixture due to conduction only as distinguished from that part due to thermal

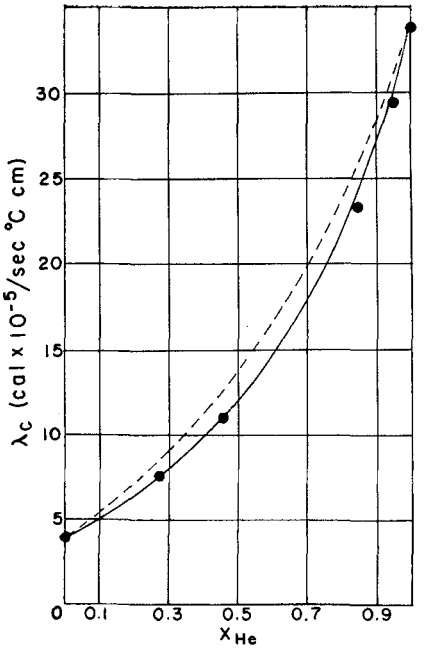

Fig. 1. Experimental and calculated conductivity of helium-argon mixtures at 0°C. Experimental data (33), ———— Equation (13), — — — — — Equation (8).

diffusion. Combining Equations (4), (6), and (7) one has

$$\lambda_c = \frac{\lambda_1}{1 + \frac{D_{11}}{D_{12}}\frac{x_2}{x_1} + \frac{D_{11}}{D_{13}}\frac{x_3}{x_1} + \cdots} + \frac{\lambda_2}{1 + \frac{D_{22}}{D_{21}}\frac{x_1}{x_2} + \frac{D_{22}}{D_{23}}\frac{x_3}{x_2} + \cdots} + \cdots = \sum_{i=1}^{n} \frac{\lambda_i}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{D_{ii}}{D_{ij}}\frac{x_j}{x_i}} \qquad (8)$$

Equation (8) involves the factor D_{ii}/D_{ij}, the experimental values of which are presently scarce. However Hirschfelder et al. and Arnold have established fairly reliable methods of estimating diffusion coefficients (*12, 1*). With the former method of determining D_{ii}/D_{ij}, Equation (8) was compared with data of binary monatomic mixtures. In all cases the calculated conductivity was found to be higher than the experimental values. A comparison of Equation (8) with the experimental data for helium-argon mixtures is shown in Figure 1.

The discrepancies between the calculated and experimental data for monatomic mixtures seemed to be a function of the molecular weight difference of the components. It appeared that a better representation of the data may be of the form

$$\lambda_c = \sum_{i=1}^{n} \frac{\lambda_i}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \left(\frac{D_{ii}}{D_{ij}}\right)^{y} \left(\frac{M_{ij}}{M_i}\right)^{z} \frac{x_j}{x_i}} \qquad (9)$$

where

$$M_{ij} = \frac{M_i + M_j}{2}$$

y and z are exponents to be determined empirically. When energy transfer occurs by collision, the exponent y and the factor $(M_{ij}/M_i)^z$ may be considered as corrections for the difference in the mean free path appropriate to diffusion and to heat conduction and for the difference of the effects of persistence of velocity upon conductivity and upon diffusion. In energy transfer by diffusion the use of a value of y other than unity and z different from zero cannot be justified on the same grounds. Hence for polyatomic molecules, in which energy transfer can be effected simultaneously by both collision and by diffusion, it seems more reasonable to assume the relations

$$\lambda_c = \sum_{i=1}^{n} \frac{\lambda_{ci}}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \left(\frac{D_{ii}}{D_{ij}}\right)^{y} \left(\frac{M_{ij}}{M_i}\right)^{z} \frac{x_j}{x_i}} + \sum_{i=1}^{n} \frac{\lambda_{di}}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{D_{ii}}{D_{ij}}\frac{x_j}{x_i}} \qquad (10)$$

$$\lambda_{ci} = \frac{2.5\, c_{vt} + 1.0\, c_r}{2.5\, c_{vt} + 1.0\, c_r + 1.32\,(c_v + c_{ir} + \cdots)}\lambda_i \qquad (11)$$

$$\lambda_{di} = \lambda_i - \lambda_{ci} \qquad (12)$$

The term $(c_v + c_{ir})$ can be obtained by subtracting $(c_{vt} + c_r)$ from the total heat capacity of component i at constant volume. Also it is convenient to note that $c_{vt} = (3/2\,R)$/mole and $c_r = 0$ for monatomic molecules, R for linear molecules, and 3/2 R for nonlinear molecules.

In writing Equation (11) it is implicitly assumed that except for the energy of translation and external rotation all other forms of energy (for example internal rotation, electronic transition, vibration, etc.) within the molecule are transferred by a diffusion mechanism. Although this is probably a fair assumption in most cases, Bromley (3) has shown that it may not be valid for easily excited internal rotations or vibrations.

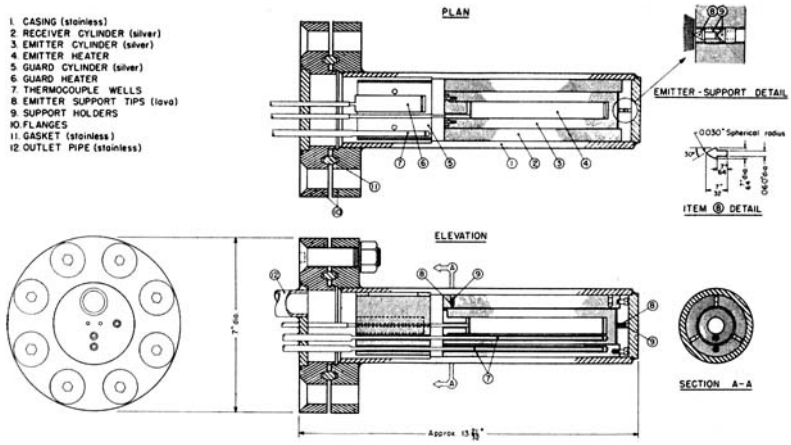

Fig. 2. Conductivity-cell assembly.

EXPERIMENTAL THERMAL CONDUCTIVITY

With a few exceptions, thermal conductivity of mixtures has been measured at or near room temperature. Data at higher temperatures are needed to test present-day theories and correlations. In the work presented here, the thermal conductivities of ten gases and of selected binary and ternary mixtures of them were determined in an apparatus essentially the same as that used by Rothman (27).

Equipment

A detailed description of the experimental work has been presented elsewhere (6). The conductivity cell assembly is shown in Figure 2. The principal components of the cell are the two concentric silver cylinders and the heat guard. The inner cylinder is supported within the outer cylinder by means of Lava* tips. The annular space between the cylinders is 0.0333 in., while the space at the bottom is 0.053 in. An electrical heater in the inner cylinder supplies the energy to be transported across the gas-filled annular space. The heat guard is a silver cylinder containing a heater that serves to prevent heat flow from the upper end of the inner cylinder. Thermocouples of 20-mil. Pt-10% PtRh were used with a high-sensitivity galvanometer

* Lava is a product of American Lava Corporation, Chattanooga, Tennessee. It is a natural stone which may be machined and then fire-hardened to a refractory.

TABLE 1. EXPERIMENTAL DATA FOR PURE GASES

Gas	T_{av}, (°C.)	$\lambda \times 10^5$, $\left(\frac{\text{cal.}}{\text{sec. °C. cm.}}\right)^*$	Literature value and source $\lambda \times 10^5$, $\left(\frac{\text{cal.}}{\text{sec. °C. cm.}}\right)$
N_2	104.5	7.459	7.58 (*20*) 7.33 (*28*) 7.25 (*27*) 7.56 (*26*)
A	106.0	5.125	5.113 (*18*) 5.16 (*20*) 5.155 (*28*)
He	100	41.94	40.75 (*17*) 41.65 (*18*) 40.86 (*20*)
O_2	101	7.732	7.90 (*17*) 7.80 (*20*)
CO_2	103	5.331	5.20 (*8*) 5.56 (*17*) 5.35 (*20*)
CH_4	98	10.60	10.86 (*17*) 10.30 (*28*)
C_3H_8	100	6.500	6.24 (*22*)
$(CH_3)_2O$	101	6.015	
Methyl formate	99	4.217	
N_2	317	10.67	10.62 (*30*) 10.77 (*20*) 10.85 (*28*)
He	315	58.73	55.58 (*18*)
CO_2	320	9.655	8.89 (*8*) 9.89 (*20*)
A	321	7.299	6.926 (*18*) 7.26 (*20*) 7.165 (*28*)
C_2H_4	318	15.30	
CH_4	317	20.34	21.00 (*20*) 18.87 (*28*)
O_2	319	11.62	11.73 (*9*)
C_3H_8	318	14.65	
$(CH_3)_2O$	318	12.96	
C_3H_8	537	25.08	
CH_4	537	25.25	

* To convert the above conductivities to (B.t.u.)/(°F.-hr.-ft.) multiply by 241.75.

and a double potentiometer for temperature measurements.

The cell is enclosed in a stainless steel casing, which may be evacuated for the purpose of determining radiant-heat transfer between the cylinders. The steel casing in turn is surrounded by an 800-lb. copper block whose large heat capacity and high heat conductivity serve to help maintain constant and uniform ambient temperature for the cell. The constant-temperature block is shown in Figure 3.

Experimental Results

Experimental conductivity was calculated from measured values of q, heat input to the inner cylinder, the corresponding temperature difference ΔT between the inner and outer cylinders, and the geometry of the cell. The relation involving these quantities is given by Rothman (*27*). To correct for accommodation coefficient effects experimental values of $\Delta T/q$ corrected for radiation were extrapolated to infinite pressure, that is to $1/p = 0$, to give the pressure independent (ideal-gas) value by the method of least squares. Figure 4 shows some typical plots of $\Delta T/q$ vs. $1/p$.

The pressure-independent data for pure gases are presented in Table 1. Available data in the literature are also shown for comparison. The latter values have been obtained in most instances from interpolation of the original data. The measurements from this work are quite consistent with those already reported, except for the value of helium at 315°C. The high conductivity was probably caused by an error in ΔT, which had a low value in this case. Experimental conductivities for binary and ternary mixtures are presented in Table 2.

The estimated probable error in the reported conductivities is 1.2%. The possible errors contributed by each of the experimental quantities required for calculating the conductivity and

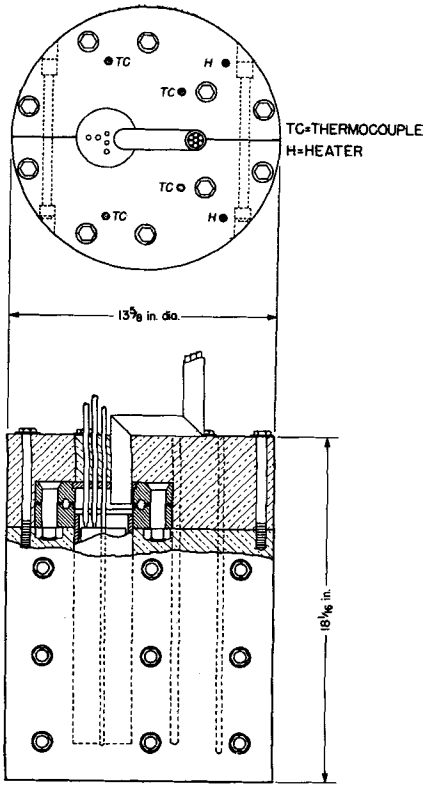

Fig. 3. Constant-temperature block.

those errors inherent in the experimental system have been discussed in detail elsewhere (*6*).

EVALUATION OF EMPIRICAL CONSTANTS FOR PROPOSED EQUATION

Because these equations are presumably approximately applicable in general, the constants in them may be evaluated from the data of any arbitrarily chosen set of binary mixtures. However the parameters appearing in these equations indicate that the data of certain systems are more desirable to use than others. For the determination of y and z in Equation (10) the most logical data to be used are those of monatomic mixtures. Because these gases do not have internal degrees of freedom, the second sum of this equation vanishes. Furthermore the factors D_{ii}/D_{ij} and M_{ij}/M_i indicate that it would be advantageous to choose mixtures whose components have widely different molecular weights. Hence the data for helium-argon mixtures were chosen. The apparent measured conductivity of a mixture λ_a is the difference between the true conductivity λ_c and the conductivity due to thermal diffusion λ_{td}. In order that the correlation will apply to all mixtures on an equal basis values of $\lambda_a - \lambda_c$, which amounted to at most 3% of λ_a, were estimated from thermal diffusion data (*6*). Existing correlations do not take into consideration thermal conductivity because of thermal diffu-

TABLE 2. EXPERIMENTAL DATA OF MIXTURES*

A. Binary Mixtures

System	x_1	T_{av}, (°C.)	$\lambda_a \times 10^5$, $\left(\frac{\text{cal.}}{\text{sec. °C. cm.}}\right)$
$He-N_2$	0.409	107.5	14.59
$He-N_2$	0.837	100	30.33
$He-N_2$	0.219	104	10.71
He-A	0.525	100.5	15.90
He-A	0.780	99	25.18
He-A	0.276	102.5	9.509
$CH_4-C_3H_8$	0.4855	95	7.636
$CH_4-C_3H_8$	0.3130	94	7.050
$CH_4-C_3H_8$	0.7792	93	8.841
$(CH_3)_2O-C_3H_8$	0.4983	95	6.180
$(CH_3)_2O-C_3H_8$	0.3149	95	6.125
$A-(CH_3)_2O$	0.4877	96	5.372
$A-(CH_3)_2O$	0.6705	96	5.183
$A-(CH_3)_2O$	0.3166	95	5.455
$CO_2-C_3H_8$	0.4490	95	5.884
$CO_2-C_3H_8$	0.6354	96	5.738
$CO_2-C_3H_8$	0.2912	95	6.083
O_2-CO_2	0.5356	96	6.365
O_2-CO_2	0.3153	96	5.865
O_2-CO_2	0.2699	97	5.777
O_2-CO_2	0.7776	97	7.027
C_3H_8-methyl formate	0.530	96	5.435
$(CH_3)_2O$-methyl formate	0.4841	97	4.928
$(CH_3)_2O$-methyl formate	0.7248	100	5.361
$(CH_3)_2O$-methyl formate	0.3059	101	4.707
He-A	0.573	316	23.00
$(CH_3)_2O$-methyl formate	0.4841	318	14.25
$A-CO_2$	0.4935	320	8.670
N_2-A	0.4966	320	8.788
$He-CO_2$	0.610	317	23.65
$He-N_2$	0.637	317	28.28
$N_2-C_2H_4$	0.4980	318	13.22
$C_2H_4-CO_2$	0.5118	318	12.69
$N_2-C_2H_4$	0.7558	319	12.05
N_2-O_2	0.3902	319	11.19
$CH_4-C_2H_4$	0.4894	317	16.73
$He-CH_4$	0.746	316	40.63
$He-CH_4$	0.550	316	30.54
$He-CH_4$	0.299	317	24.58
$He-N_2$	0.305	318	16.27
$He-N_2$	0.739	316	33.47
He-A	0.306	318	13.36
He-A	0.774	316	33.23
$C_3H_8-(CH_3)_2O$	0.4966	317	13.78
$N_2-C_3H_8$	0.5253	318	13.06
$A-C_3H_8$	0.4712	318	11.86
$N_2-C_3H_8$	0.4761	538	20.99
$A-C_3H_8$	0.4712	538	19.80
CH_4-A	0.4767	538	17.03

* Numerical subscripts denote components in the order in which they appear in the tables.

TABLE 2. EXPERIMENTAL DATA OF MIXTURES

B. Ternary Mixtures

System	x_1	x_2	T_{av}, (°C.)	$\lambda_a \times 10^5$, $\left(\frac{\text{cal.}}{\text{sec. °C. cm.}}\right)$
$He-N_2-A$	0.415	0.468	99.5	13.95
$N_2-O_2-CO_2$	0.3231	0.3729	97	6.729
$A-(CH_3)_2O-C_3H_8$	0.3660	0.3260	98	5.767
$He-CH_4-N_2$	0.159	0.365	317	16.74
$A-C_3H_8-(CH_3)_2O$	0.5348	0.2310	318	11.01

sion (9). It was found that the best values of y and z are approximately 1 and 1/8, respectively. With the introduction of these constants Equation (10) becomes

$$\lambda_c = \sum_{i=1}^{n} \frac{\lambda_{oi}}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{D_{ii}}{D_{ij}} \left(\frac{M_{ij}}{M_i}\right)^{1/8} \frac{x_j}{x_i}} + \sum_{i=1}^{n} \frac{\lambda_{di}}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{D_{ii}}{D_{ij}} \frac{x_j}{x_i}} \quad (13)$$

A comparison of this expression with the data of helium-argon mixtures at 0°C. is shown in Figure 1.

COMPARISON OF CORRELATION WITH EXPERIMENTAL DATA

In comparing conductivity data with Equation (13) it is convenient to classify molecules according to the following scheme: Type I, monatomic molecules; Type II, rotators without energy of vibration or internal rotation; Type III, molecules having energies of vibration and (or) internal rotation and hydrogen. Hydrogen is classified as Type III because its energy of rotation is known to be transferred by diffusion (15).

Monatomic Mixtures

It is with this type of mixtures that the effects of molecular weight and temperature upon the conductivity can be best assessed, because these gases possess only translational kinetic energy and their intermolecular forces should be quite similar. Equation (13) indicates that binary mixtures of this type should exhibit conductivity vs. mole-fraction curves lying below the linear relation, because both D_{ii}/D_{ij} and M_{ij}/M_i (where i refers to the lighter component) are larger than unity; that is the contribution of the lighter component to mixture conductivity is less than the product of its mole fraction and conductivity. This reduction is usually not balanced by the increase in the contribution of the heavier molecule. The net result is negative deviation from the linear relation.

Temperature may influence the conductivity of monatomic mixtures by affecting the ratio D_{ii}/D_{ij} and the conductivity of the pure gases. D_{ii}/D_{ij} should be only slightly dependent on temperature. The conductivity of monatomic gases can be represented quite well over temperature ranges of several hundred degrees by bT^n with a value of n between 0.5 and 1. If D_{ii}/D_{ij} were assumed constant, and the n values for all components of a mixture were equal, then the ratio of the actual conductivity of the mixture

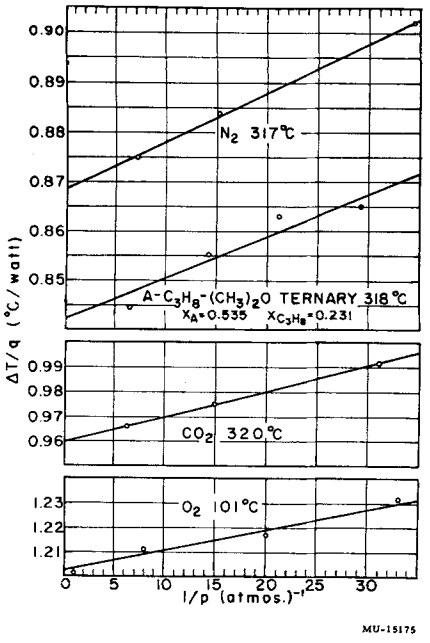

Fig. 4. Accommodation effect.

to that calculated from the simple mixing rule λ_c/λ_1 would be independent of temperature (6). If the n values were different, then λ_c/λ_1 would be a function of $T^{n'-n''}$.

A comparison of the conductivity data of helium-argon mixtures with Equation (13) has been made in the light of the foregoing points. In this case the difference between the n values is 0.15 over the temperature range of 200° to 800°K., and the variation of $T^{(n'-n'')}$ is small. The data for binary mixtures in the temperature range of 0° to 316°C. presented in Figure 5 demonstrate that λ_c/λ_1 is nearly independent of temperature as expected.

Mixtures Containing Molecules of Types I and II

Molecules of Type II have rotational energy in addition to translational kinetic energy. Both kinds of energy are transferred rapidly by collision (3, 32). Therefore when Equation (13) is applied to mixtures of this group, the second sum does not appear; that is the expression for the conductivity of these mixtures is identical with that for monatomic mixtures. Mixtures of helium and nitrogen may be taken as representatives of this group. Over the temperature range of 170° to 670°K., $n' - n''$ in this case is 0.22; hence λ_c/λ_1 should be only weakly dependent upon temperature, as shown in Figure 6.

Mixtures Containing Molecules of Type III

Among molecules of this type the hydrogen molecule is of special interest in two respects. First, its lightness gives rise to mixtures having very high molecular-weight ratios. Second, its rotational energy and translation kinetic energy are transferred by different processes, diffusion and collision, respectively (15). Thus mixtures containing hydrogen serve to test Equation (13) not only for the proper relation between molecular-weight differences and conductivity but also for the assumption that molecular energy may be separated into collisional and diffusional parts. A comparison of the experimental and calculated values of the conductivity of mixtures of hydrogen and argon is shown in Figure 7. These are the simplest mixtures in which energy transport by diffusion occurs, as the only other form of energy possessed by the molecules is translational kinetic energy. Further, the effect of molecular-weight difference upon the conductivity of these mixtures should be very pronounced. The agreement between Equation (13) and the data is seen to be good; the average deviation is 1.5%. When however the rotational energy of hydrogen is considered to be transferred by collision, as in the case of nitrogen discussed above, the agreement is poorer; the average deviation becomes 3.3%. The procedure of separating the rotational and translational energies of hydrogen appears to be justified. Similar results have also been obtained in comparing the conductivity of mixtures of hydrogen and carbon dioxide with Equation (13).

In theory the result of splitting the energy into two parts can be best demonstrated in mixtures of molecules of Type III other than hydrogen because many of these molecules may have more than half their energy distributed in the vibrational degrees of freedom at temperatures conveniently attainable experimentally. Unfortunately, in comparison of Equation (13) with the available data on mixtures of these Type III molecules, it is difficult to justify the procedure of

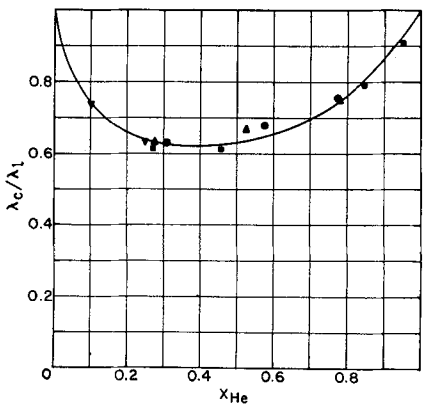

Fig. 5. Temperature effect on λ_c/λ_1 of helium-argon mixtures. ■ Experimental, 0°C., Wachsmuth (33); ▲ Experimental, 100°C., this work; ● Experimental, 316°C., this work; ▼ Calculated, 100°C., Equation (13).

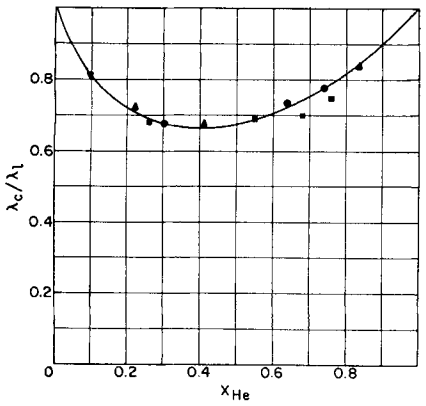

Fig. 6. Temperature effect on λ_c/λ_1 of helium-nitrogen mixtures. ■ Experimental, 0°C., Davidson and Music (7); ▲ Experimental, 104°C., this work; ● Experimental, 316°C., this work; ▼ Calculated, 100°C., Equation (13).

splitting the energy transport into collisional and diffusional portions. In accordance with this relation the difference in the effective contributions of the two kinds of energy of a molecule to the conductivity of a mixture depends upon the empirical factor $(M_{ij}/M_i)^{1/8}$. Unless the molecular weights of the components of the mixture are widely different, this factor is near unity, in which case there is little distinction in effective contribution between the two types of energy transport. Indeed, calculations have shown that the conductivity of these mixtures can be correlated nearly equally well by the expression

$$\lambda_c = \sum_{i=1}^{n} \frac{\lambda_i}{1 + \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{D_{ii}}{D_{ij}} \left(\frac{M_{ij}}{M_i}\right)^{1/8} \frac{x_j}{x_i}} \qquad (14)$$

Appreciable differences between the values calculated with this expression and with Equation (13) would appear only in cases where not only the molecular-weight ratio is high but also the diffusional contribution is a significant portion of the mixture conductivity. For example experimental data for mixtures of heavy monatomic gases with CH_4 are expected to lend support to Equation (13).

Percentage Deviation from Data

A comparison of Equation (13) with data from the literature and those of this work was made for 177 points from thirty different nonpolar binary systems in temperatures ranging from 0° to 774°C.* The average deviation of Equation (13) from all the data is 2.1%. Comparisons of predicted val-

* Tabular material has been deposited as document 7080 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

Table 3. Comparison of Experimental and Calculated Conductivities of Binary Mixtures According to Data Source

Data source	Number of points	Equation (13) % deviation Average	Maximum
Collected by Lindsay and Bromley (*21*)	68	1.97	10.47
This work	37	1.59	5.30
Rothman (*27*) N_2-CO_2	23	2.88	4.95
Keyes (*19*) N_2-CO_2	12	2.14	4.62
Srivastava and Saxena (*29*)	22	1.90	4.55
Davidson and Music (*7*)	15	2.80	5.59
Total	177	2.08	10.47

ues and experimental data are presented according to data source in Table 3. Data for sixteen ternary mixtures at temperatures from 0° to 317°C. are given in Table 4. The average deviations of Equation (13) from these data is 2.2%.

The Effect of Temperature Upon Mixtures Containing Vibrators

It is well established experimentally that the conductivity of mixtures of nitrogen and carbon dioxide shows a positive deviation from the simple mixing rule at temperatures above 150°C. and a negative deviation at lower temperatures (*27, 19*). The data of this work show that the deviation is also positive for the following systems: A-CO_2, N_2-C_3H_8, A-C_3H_8, C_2H_4-CO_2, and N_2-C_2H_4 in the neighborhood of 320°C.; CH_4-A, N_2-C_3H_8, and A-C_3H_8 at 538°C.; and CO_2-C_3H_8 at 95°C. A similar trend is also seen in the data for the C_2H_4-air mixtures at 20° and 65°C. (*10*).

That mixtures of nonpolar molecules should behave in this manner has not been heretofore satisfactorily explained. However these experimental facts appear to be consistent with predictions based upon Equation (13). It was that for molecules having only translational and rotational energies the percentage deviation from a linear relation is nearly independent of temperature. Furthermore the contribution of the lighter components, which have higher conductivity, is reduced by the lowered persistence of velocity in their collisions with heavier molecules, and similarly the contribution of the heavier molecules is increased. The net result is a negative deviation from the linear relation. Now, if the heavier molecule made a diffusional contribution to energy transport, this contribution would be greater in a mixture with a lighter molecule than in itself because its rate of diffusion would be raised. This diffusional contribution then tends to offset the negative deviation caused by collisional transfer, provided the lighter molecule possesses little or no energy that is transported by diffusion. With increasing temperature the diffusion contribution rises, and the conductivity of the mixture shifts from a negative to a positive deviation. The data cited at the beginning of this para-

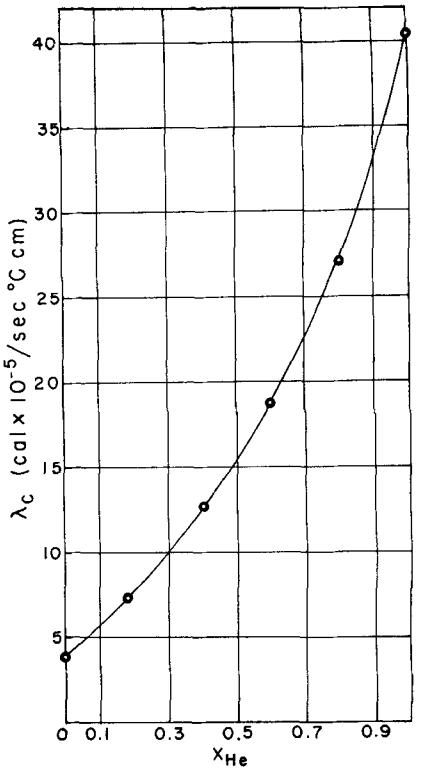

Fig. 7. Experimental and calculated conductivity of hydrogen-argon mixtures at 0°C. ○ Experimental data (*16*), ———— Equation (13).

Table 4. Comparison of Experimental and Calculated Conductivities of Ternary Mixtures

System and data source	Temp., (°C.)	x_1	x_2	λ_1 (cal. × 10^{-5}/sec. °C. cm.)	λ_2	λ_3	λ_a	λ_c	$\lambda_{calc'd.}$ [Eq. (13)]	Deviation, (%)
He-CH_4-O_2 (*2b*)	0	0.743	0.060	33.86	7.20	5.77	20.0	20.15	20.93	+3.87
		0.712	0.100				19.5	19.66	19.88	+1.12
		0.684	0.135				18.6	18.77	19.00	+1.22
A-CH_4-O_2 (*2b*)	0	0.751	0.050	3.89	7.20	5.77	4.59	4.59	4.423	−3.64
		0.712	0.100				4.71	4.71	4.568	−3.01
		0.677	0.144				4.91	4.91	4.703	−4.21
Ne-A-Kr (*29*)	38	0.1387	0.717	11.80	4.38	2.23	4.50	4.506	4.628	+2.71
		0.1861	0.145				3.47	3.484	3.504	+0.57
		0.3019	0.385				4.80	4.816	4.948	+2.74
		0.4537	0.157				5.45	5.471	5.471	0
		0.4984	0.130				6.58	6.60	6.782	+2.75
		0.1279	0.157				3.24	3.251	3.251	0
		0.7919	0.142				8.45	8.46	8.971	+6.03
N_2-O_2-CO_2 (this work)	97	0.3231	0.3129	7.331	7.660	5.218	6.729	6.729	6.760	+0.46
He-N_2-A (this work)	99.5	0.415	0.468	41.90	7.374	5.052	13.95	14.17	14.21	+0.28
He-CH_4-N_2 (this work)	317	0.159	0.365	55.6	20.33	10.67	16.74	16.94	17.51	+3.36
Average deviation (16 points)										2.2
Maximum deviation										6.0

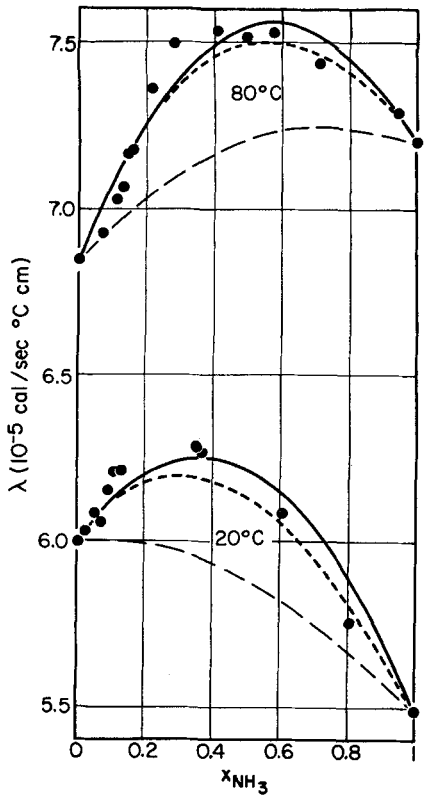

Fig. 8. Experimental and calculated conductivity of ammonia-air mixtures. • Experimental data (*10*), - - - - - Lindsay-Bromley correlation, ———— Equation (13) and modified Arnold equation, — — — — — Equation (13) and original Arnold equation.

graph and other data which were examined appear to support this argument, because in every case involved the composition is such that the component having the higher diffusional contribution also has a higher diffusion rate in the mixture than in itself.

Conductivity of Polar-Nonpolar Mixtures

In the application of Equation (13) to nonpolar mixtures the method of Hirschfelder et al. was used to calculate the ratio D_{ii}/D_{ij} (*12*). Such a procedure cannot be used for mixtures containing polar molecules; therefore a modification of Arnold's method was used (*1*). Accordingly D_{ii}/D_{ij} for these mixtures was computed by the expression

$$\frac{D_{ii}}{D_{ij}} = \left(\frac{M_i}{M_{ij}}\right)^{\frac{1}{2}} \left\{\frac{1}{2}\left[1+\left(\frac{V_j}{V_i}\right)^{\frac{1}{3}}\right]\right\}^2 \left[\frac{T + 0.733\,F\,1.5(\sqrt{T_{bi}\,T_{bj}})}{T + 1.5\,T_{bi}}\right] \quad (15)$$

The factor 0.733 was introduced by Gruss and Schmick to calculate the mean Sutherland's constant for a polar-nonpolar pair of molecules (*10*).

The conductivities of mixtures of ammonia and air at 20 and 80 deg. were calculated with D_{ii}/D_{ij} from Equation (15) and from Arnold's original equation. The results of these calculations and the experimental data shown in Figure 8 demonstrate that modification of Arnold's equation improves the predictions for this system. Equation (15) is therefore recommended for the polar nonpolar interactions in multicomponent mixture calculations.

Examination of the conductivity data of mixtures of this type reveals that in all cases there is a positive deviation from the simple mixing rule. Vine and Bennett pointed out that the cause for this behavior is that when polar molecules are mixed with nonpolar ones, the former should have an effective conductivity larger than in the pure state, because in polar-nonpolar collisions the polar molecules should behave effectively as nonpolar molecules (*31*). Calculations show that Equations (13) and (15) are consistent with this qualitative aspect of the conductivity vs. composition curves for mixtures of this type. Calculated values and experimental data were compared for forty-nine mixtures of nine different binary systems in temperatures from 0° to 121°C.* The average deviation of Equation (13) from the data is 2.2%.

Estimation of D_{ii}/D_{ij} from Viscosity. It is of interest that for nonpolar molecules D_{ii}/D_{ij} can be shown equal to the ϕ_{ij} used in gas mixture viscosity calculations (*34*). Hence the equations for ϕ_{ij} and the charts which are available for convenient reading of

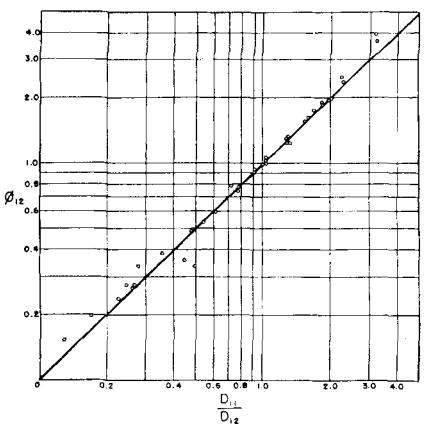

Fig. 9. Correlation between ϕ_{12} and D_{11}/D_{12}.

ϕ_{ij} from the viscosities and molecular weights of the pure components (*4*) can be used in thermal conductivity calculations. Validity of these relationships for a binary system may be determined as follows. The expression for the binary diffusion coefficient in terms of the coefficient of self-diffusion in the case of hard spherical molecules is approximately

$$D_{12} = \frac{\frac{4}{\sqrt{2}}\left(\frac{M_1+M_2}{M_1 M_2}\right)^{1/2}}{\left[\left(\frac{1}{D_{11}^2 M_1}\right)^{1/4} + \left(\frac{1}{D_{22}^2 M_2}\right)^{1/4}\right]^2} \quad (16)$$

Therefore

$$\frac{D_{11}}{D_{12}} = \frac{\left[\left(\frac{1}{M_1}\right)^{1/4} + \left(\frac{D_{11}}{D_{22}}\right)^{1/2}\left(\frac{1}{M_2}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left(\frac{M_1+M_2}{M_1 M_2}\right)^{1/2}} \quad (17)$$

Following Wilke (*34*) one assumes

$$\frac{D_{11}\,\rho_1}{\eta_1} = \frac{D_{22}\,\rho_2}{\eta_2} \quad (18)$$

Combining Equations (17) and (18) and expressing the result in general form for components i and j of a mixture one gets

$$\frac{D_{ii}}{D_{ij}} = \frac{\left[1+\left(\frac{\eta_i}{\eta_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}}\left[1+\frac{M_i}{M_j}\right]^{1/2}} \equiv \phi_{ij} \quad (19)$$

The correlation between ϕ_{ij} and D_{ii}/D_{ij} calculated on the basis of the first approximation by the Lennard-Jones 6-12 model is shown in Figure 9. The points fall fairly close to the 45-deg. line. In view of the fact that molecules are not really hard spheres and hence

* See footnote on page 225.

the group $\rho D/\eta$ is not constant, the correlation is about as good as can be expected.

CONCLUSIONS

From the kinetic theory and a number of empirical assumptions, equations have been developed to relate the thermal conductivity of gas mixtures to the diffusion coefficients and other properties of the component gases. These equations have been found to be in qualitative agreement with the experimental facts. With slight empirical modifications they have been made to conform with experimental data, although their formal identity is no longer preserved. In accordance with the proposed relations the ratio λ_c/λ_t for very simple molecules should be approximately constant within rather wide temperature limits. It has been shown that available experimental data support this prediction.

These equations are applicable to both nonpolar and polar-nonpolar mixtures. In the former case calculation of the diffusivity ratio according to the method of Hirschfelder et al. appears to be satisfactory in spite of the fact that the individual diffusivities calculated this way deviate, on the average, 6% from the experimental values (*12*). For polar-nonpolar mixtures the suitability of a modified Arnold's equation for calculating these ratios has been demonstrated.

It should be noted that the proposed correlation has been tested against data for mixtures of rather simple molecules. Very long or complex molecules that may intercoil or stick during collision have not been considered. Also, systems involving chemical reactions have been excluded. Furthermore, all the data for comparison were taken at pressures less than those having an effect upon conductivity or viscosity. Additional data at substantially higher temperatures would be desirable to test further the hypothesis of energy splitting into collisional and diffusional contributions to the transport mechanism.

NOTATION

c_{ir} = internal rotational heat capacity
c_r = rotational heat capacity
c_{vt} = translational heat capacity at constant volume
c_v = vibrational heat capacity
C_v = heat capacity at constant volume
D = diffusion coefficient (sq.cm./sec.)
D_{11} or D_{ii} = self-diffusion coefficient
D_{12} or D_{ij} = binary diffusion coefficients
D_{1m} = diffusion coefficient given by Equation (5)
F = a numerical factor which is a function of the ratio of molecular volumes, V
M = molecular weight
p = pressure (atm. or mm. Hg)
q = heat flow (cal./sec., w., or B.t.u./hr.)
R = universal gas constant
T_{av} = average temperature between inner and outer cylinders of the cell
T_{bi} = normal boiling temperature of component i (°K.)
Δ_T = temperature difference (°C.)
v = root-mean-square velocity of molecules
V_i = molecular volume of the ith component in the liquid state at the boiling point
x_i = mole fraction of the ith component

Greek Letters

η = viscosity (poises)
η_i = viscosity of the ith component
Λ = mean free path of molecules (cm.)
λ = thermal conductivity (cal./cm. sec. °C.)
λ_i = thermal conductivity of the ith component
λ_{im} = effective thermal conductivity of the ith component in a mixture
λ_a = apparent measured thermal conductivity
λ_c = conductivity of a gas mixture from conduction only
λ_t = conductivity of a mixture calculated by the simple mixing rule; that is $\lambda_t = x_1 \lambda_1 + x_2 \lambda_2$
λ_{ci} = collisional conductivity of the ith component [Equation (10)]
λ_{di} = diffusional conductivity of the ith component [Equation (10)]
ρ = density of a gas (g./cc.)
ρ_i = density of the ith component
ρ_{im} = density of the ith component in a mixture

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